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NATURAL ATTENUATION OF CHLORINATED SOLVENTS IN SUBARCTIC GROUND WATER

A

THESIS

Presented to the Faculty

of the University of Alaska Fairbanks

in Partial Fulfillment of the Requirements

for the Degree of

DOCTOR OF PHILOSOPHY

By

Sharon Alice Richmond, M.S.

Fairbanks, Alaska

May 2001

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ABSTRACT

Little is known about natural attenuation of chlorinated solvents in subarctic ground water. This study aimed to better understand the biogeochemistry and microbiology associated with naturally occurring processes of contaminant removal at two hydrologically diverse sites near Fairbanks, Alaska. Six Mile Village, located several km north of the Tanana River, is hydrologically stable, experiencing minor fluctuations in ground-water levels. Fort Wainwright is located adjacent to the Chena River and is hydrologically dynamic, experiencing seasonal flow reversals and substantial fluctuations in water-table elevations. By comparing data collected seasonally and with data collected at the two sites, I determined how ground-water/surface-water interactions affected in situ redox conditions and, hence, natural attenuation processes. A portion of the aquifer at Fort Wainwright was undergoing active treatment so I was also able to compare differences in chlorinated solvent transformations in treated and untreated ground water. Although ground water at Fort Wainwright was generally more oxidized than ground water at Six Mile Village, hydrogen concentrations at both sites were almost uniformly within ranges suggestive of iron or manganese reduction. However, aquifer sediments in the Tanana/Chena Alluvium are composed of mafic (containing reduced iron and manganese) minerals; suspended ferric iron appeared to result from oxidation of ferrous iron as ground water rose through the unsaturated zone. Sulfate concentrations were substantial and dissolved sulfide in most samples suggested that sulfate reduction might have been an important process. Calculated in situ Gibbs free energies for iron and

sulfate reduction were energetically favorable at both sites; given other geochemical data, it seems likely these two processes co-occurred. Although methane was present in most samples, methanogenesis from H_2/CO_2 was generally not energetically feasible at either site. Methane likely diffused from underlying permafrost or peat. The presence of less chlorinated intermediates of solvent degradation suggested that biological reductive dechlorination occurred, providing further support that sulfate-reducing conditions existed. However, low rates of microbial activity, incomplete degradation and persistence of contaminants imply that biologically mediated mechanisms did not likely represent an important contribution to natural attenuation of contaminants at either site where dilution appeared to be a major attenuation mechanism.

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INTRODUCTION

Over the past decade, natural attenuation has been chosen as the preferred cleanup strategy at an increasing number of contaminated sites in the United States. Natural attenuation encompasses all physical, chemical, and biological processes that, without human intervention, cause a reduction in mass and concentration of environmental contaminants. Physical processes include advection and dispersion, dilution, volatilization, and sorption. These processes either increase or retard contaminant movement in the subsurface and do not result in contaminant transformation. Chemical processes, however, such as abiotic reductive dechlorination, may result in structural changes to contaminants. Several studies have addressed abiotic transformations of chlorinated aliphatics through interactions with dissolved metals although in most systems, these reactions may be quite slow (Vogel et al., 1987). On the other hand, biological processes offer the most promising means of completely removing environmental contaminants within reasonable time frames, although, which of a wide variety of potential contaminant transformation processes may occur is highly dependent on ambient redox conditions.

Trichloroethene (TCE), a widely used solvent and degreaser typical of a class of compounds known as chlorinated aliphatics, is one of the most common ground-water contaminants in the U.S. today (NRC, 2000). Because TCE and some of its decay products are known or suspected carcinogens (Federal Register, 1989), its removal from ground water is a subject of interest. As mentioned previously, in situ redox conditions (described by predominant terminal electron-accepting processes (TEAPs) determine

which biological processes may occur in contaminated ground water. In highly anaerobic systems (sulfate-reducing to methanogenic), TCE can serve as an electron acceptor for some bacteria. This process, known as biological reductive dechlorination, occurs during oxidation of another carbon source and produces cis- and/or trans-1,2-dichloroethene (cis- or trans-DCE, respectively); the presence of higher quantities of the cis isomer is generally accepted as evidence of biological reductive dechlorination (NRC, 2000). Continued dechlorination produces vinyl chloride (VC), and ethene (Vogel et al., 1987). The extent to which these dechlorination reactions may proceed is dependent upon ambient TEAPs. Under sulfate-reducing conditions, DCE tends to accumulate whereas under methanogenic conditions, VC, a potent human carcinogen, may accumulate; neither condition is desirable and it is only under the most severely reducing conditions that complete dechlorination to ethene is observed (NRC, 2000). In less reduced environments, some bacteria can mineralize partially dechlorinated TCE transformation intermediates using a variety of electron acceptors (e.g., Fe(III) (Bradley and Chapelle, 1996; 1997), Mn(IV) (Bradley et al., 1998), and oxygen (Davis and Carpenter, 1990)). In aerobic systems, TCE, DCEs, and VC can be co-metabolized during biological oxidation of another compound (e.g., methane, toluene, or phenol (Vogel et al., 1987)). This co-metabolism of TCE does not result in the production of DCEs or VC. Instead, aerobic co-metabolic processes form highly unstable epoxides that spontaneously hydrolyze into benign end products (including chloroacetate, glyoxylate, formate, and carbon monoxide) (Hou et al., 1983; Henry and Grbić-Galić, 1989; Oldenhuis et al., 1989). Clearly, many naturally occurring reactions are potentially capable of removing chlorinated solvents

from ground water and although natural attenuation has been a successful treatment strategy at a number of sites in temperate climates, its applicability is unproven in subarctic environments.

When natural attenuation is not a suitable treatment strategy, the physical process of air injection with soil vapor extraction (AI/SVE) is sometimes chosen as a means of active treatment. Because air injection increases ground-water dissolved oxygen, it is generally assumed that biological reductive dechlorination—a strictly anaerobic process—will not occur in ground water being treated with this method. However, reductive dechlorination has been demonstrated in an aerobic sediment column (Enzien et al., 1994) and in an expanded-bed bioreactor (Phelps et al., 1991), both of which were designed to assess the utility of a methanotrophic consortium for the biological removal of tetrachloroethene (PCE), TCE and mixed organic wastes. These studies suggested that anaerobic degradation of PCE and TCE could produce less chlorinated intermediates, which could then be available for aerobic mineralization via methanotrophic co-metabolism. Results of these laboratory studies demonstrated that unexpected 'enhanced bioremediation' processes could occur during active treatment. Part of the research described in this thesis addresses differences in transformation mechanisms between untreated and treated (AI/SVE) subarctic ground water.

Because in situ redox conditions dictate rates and extent of contaminant degradation, an accurate determination of in situ TEAPs is an essential component of any natural attenuation feasibility study. Monitoring temporal and spatial distribution of electron acceptors (i.e., ferric iron, sulfate, carbonate) and reduced end products (i.e.,

ferrous iron, sulfide, and methane) can give investigators useful information regarding in situ redox conditions (Baedecker and Back, 1979a,b). For example, increased concentrations of dissolved sulfide coupled with decreased concentrations of sulfate in the core of a contaminant plume are solid evidence that sulfate reduction is an important natural attenuation process. However, this determination is not always so straightforward. Reduced products of terminal metabolism can migrate to down-gradient portions of contaminant plumes (Christensen et al., 2000) or readily precipitate out of solution with dissolved iron (Cozzarelli et al., 2000). Additionally, electron acceptors may be replenished from mineral sources (Plummer et al., 1990) or confining-bed pore water (Chapelle and McMahon, 1991) and depletion may not be observed. This situation exists in Fairbanks ground water where sulfate concentrations fluctuate temporally and substantial concentrations of dissolved iron may cause precipitation of sulfide produced during sulfate reduction (Hinzman et al., 2000).

The currently accepted method of identifying in situ TEAPs couples measurement of dissolved hydrogen with the spatial distribution of electron acceptor concentrations and reduced products of terminal metabolism (Chapelle et al., 1995). The use of hydrogen concentrations as indicators of terminal metabolic processes in aquatic sediments was first suggested by Lovely and Goodwin (1988). This method is based upon the premise that terminal metabolic bacteria will maintain steady-state hydrogen concentrations at a level characteristic of each individual TEAP due to the competitive exclusion of other TEAPs; TEAPs with a lower affinity for hydrogen (e.g., can obtain useful amounts of energy per reaction at lower hydrogen concentrations) will exclude

other terminal metabolic processes by maintaining hydrogen concentrations as low as is energetically feasible. However, because the ultimate energy yield of all TEAPs is controlled by the thermodynamics of the reaction and may, therefore, be affected by solute activities (Hoehler et al., 1998) and temperature (Westermann, 1994), empirically derived hydrogen concentrations reportedly indicative of individual TEAPs may not accurately reflect in situ TEAPs in all environments.

Jakobsen et al. (1998) first suggested the use of TEAP energetics to ascertain which terminal metabolic reactions were energetically feasible within contaminant plumes. In their study, they used calculated in situ Gibbs free energies of reaction to demonstrate that concurrent iron and sulfate reduction, and at some points, methanogenesis, were energetically feasible in a landfill-leachate plume. This approach, previously used only in laboratory experiments, was later applied successfully at another pristine site (Jakobsen and Postma, 1999). One of the advantages of this approach is that it may be useful when addressing the potential for biodegradation of environmental contaminants (Christensen et al., 2000). Application of this method at subarctic and other sites may provide useful information for future studies.

All research described in this thesis was undertaken to examine natural attenuation processes in subarctic ground water and to assess the utility of currently used methods of contaminant-plume characterization in subarctic environments. These studies addressed 1) the applicability of empirically-derived hydrogen concentrations as indicators of in situ TEAPs; 2) hydrogeochemistry and microbiology associated with natural attenuation of low concentrations of chlorinated ethenes; 3) the effects of transient

ground-water flow on natural attenuation processes; and 4) differences in natural attenuation mechanisms in treated (AI/SVE) and untreated ground water. Because information regarding natural attenuation of TCE and in situ TEAPs in subarctic ground water is very limited, the research described within this thesis will provide useful information for regulators and managers of contaminated subarctic sites and a framework for future study.

CHAPTER 1

Geochemistry and microbiology associated with TCE transformation in treated and untreated subarctic ground water[1]

Abstract

The effects of hydrology, geochemistry, and microbiology on trichloroethene (TCE) degradation were examined in treated (aerobic) and untreated (anaerobic) ground water. Natural attenuation of TCE may occur in aerobic or anaerobic subsurface systems by several processes, all of which are dependent upon ambient reduction potential. Air injection with soil vapor extraction (AI/SVE) caused increased dissolved oxygen (DO) at treated wells. However, concentrations of sulfide were consistently higher in treated ground water, suggesting that plugging of aquifer solids may have created anaerobic zones within the treatment area. The likely cause of plugging was oxygenation of anaerobic ground water, which led to the precipitation of iron hydroxides and increased biomass. Production of *cis*-1,2-dichloroethene (*cis*-DCE) near spargers indicated biological reductive dechlorination; in untreated ground water, near equal quantities of *cis*- and *trans*-DCE suggested other dechlorination mechanisms. Vinyl chloride was not detected in any samples. Hydrogen concentrations in untreated ground water were generally within or below the range predicted for Fe(III)-reduction ($\leq 0.1 - 0.8$ nM),

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although other geochemical data suggested that sulfate reduction also occurred. Methane concentrations were < 1 to 60 μg/L and numbers of methanotrophic bacteria were greater in treated ground water; cometabolic activity may have occurred there. Methanotrophs were not detected in untreated ground water. TCE and DCE concentrations decreased during this study due to a combination of active treatment and advective/dispersive mechanisms. However, it is likely that biological transformations and perhaps methanotrophic cometabolism contributed to TCE transformation in treated and untreated ground water.

Keywords: Ground water; Natural attenuation; TCE; Petroleum hydrocarbons; Microbiology; Subarctic

1.1. Introduction

Trichloroethene (TCE), a widely used solvent and degreaser, is a common ground-water contaminant in the U.S. TCE and some of its decay products are known or suspected carcinogens (Federal Register, 1989), so its removal from ground water is a subject of interest. Various treatment strategies exist for remediation of TCE contamination. Over the past decade, monitored natural attenuation has been chosen as a remediation strategy at many sites (National Research Council (NRC), 2000). This approach involves the long-term monitoring of contaminant concentrations and the various biological, chemical and physical factors associated with contaminant loss.

Natural attenuation of TCE may occur in aerobic or anaerobic subsurface systems by several processes, all of which are dependent upon prevailing terminal electron-

accepting processes (TEAPs). Under sulfate-reducing or methanogenic conditions, TCE can serve as an electron acceptor for chlororespiring bacteria or undergo cometabolic reductive dechlorination by sulfate reducing bacteria (Löffler et al., 1999 and references cited therein). These processes occur during oxidation of an electron donor (e.g., carbon source or hydrogen) and sequentially produce *cis*- and/or *trans*-1,2-dichloroethene (DCE), vinyl chloride (VC), and ethene (Vogel and McCarty, 1985). The presence of greater quantities of the *cis* isomer is generally indicative of biological activity. Under sulfate-reducing conditions, dechlorination may stall at DCE; in highly reducing environments (methanogenic), ethene may be produced (NRC, 2000). In less reduced environments, other bacteria can mineralize TCE transformation intermediates using a variety of electron acceptors (e.g., Fe(III) (Bradley and Chapelle, 1996, 1997), Mn(IV) (Bradley et al., 1998), or oxygen (Davis and Carpenter, 1990)). TCE, DCEs, and VC can also be aerobically cometabolized during oxidation of a primary substrate (e.g., methane, toluene, or phenol), resulting in the formation of unstable epoxides that decompose into benign end products (Vogel et al., 1987). Several studies have addressed abiotic reductive dechlorination of chlorinated ethenes via by transition metals, though in most systems these reactions may be quite slow (Vogel et al., 1987 and references cited therein).

At the site examined in this study, substantial quantities of petroleum hydrocarbons existed in soil and ground water. Active treatment via air injection with soil vapor extraction (AI/SVE) was chosen as a means of treating of this contamination. During operations associated with AI/SVE, TCE contamination was also found in the area. Since air injection generally increases dissolved oxygen (DO) concentrations in

treated ground water, it follows that biological reductive dechlorination will be inhibited in ground water treated with this method. However, reductive dechlorination has been demonstrated in an aerobic sediment column (Enzien et al., 1994) and in an expanded-bed bioreactor (Phelps et al., 1991), both of which were designed to assess the utility of a methanotrophic consortium for the biological removal of tetrachloroethene (PCE), TCE and mixed organic wastes. These studies suggested that anaerobic degradation of PCE and TCE could occur in localized, anaerobic microenvironments, thereby producing DCE and VC, which could then be mineralized aerobically via direct oxidation or methanotrophic cometabolism.

This study compared TCE transformation in treated (AS/SVI) and untreated ground water. We examined how intermittent oxygenation of ground water affected ground-water geochemistry and microbiology and, in turn, what effects these parameters may have had on natural attenuation processes in a subarctic aquifer.

1.2. Materials and Methods

1.2.1. Site Description and Past Practices

Thorough descriptions of site history and past practices have been previously published (CH2M Hill, 1994, 1996). Building 1060 is located on Fort Wainwright, an Army facility near Fairbanks, Alaska, and is situated approximately 100 m south of the Chena River, (Fig. 1 a-b). Over the past 50 years, the immediate area has been used for a variety of activities including a dry cleaning facility, a decontamination station and a rifle range, all of which have since been discontinued. In addition, the site was previously

used as a gasoline fill station and fuel storage facility; two large abandoned underground gasoline storage tanks (UST) used in the 1940s have been removed (date unknown) (Fig.1b). In 1990, a 3,800-L diesel UST located directly beneath 6386 (Fig. 1b) was also removed. Remedial investigations for gasoline and diesel contamination in the soil and ground water began in 1990. The area surrounding Building 1060 represents the downgradient portion of a very large diesel- and gasoline-range organics plume (DRO and GRO, respectively). In 1993, an estimated 33,000 kg of contaminant was present in soil (DRO) and ground water (DRO and GRO) between the Chena River and Gaffney Road (about 50 m south of Building 1060), with the bulk of contamination located directly south and east of the area shown in Figure 1b (CH2M Hill, 1994). By April 1995, ground-water DRO and GRO concentrations approached lower detection limits just north of Building 1060 although soil concentrations were higher, approximately 5 mg/kg in soil borings collected near monitoring well 6386. By September 1993, concentrations of benzene, toluene, ethylbenzene and xylenes (BTEX) were below detection limits in most ground-water samples (CH2M Hill, 1994). In 1993, a worker discovered an overturned 5-gallon (about 19 L) TCE container next to monitoring well 6386 (Fig 1b) although amounts of TCE later recovered indicate that this was not the only source; TCE and DCE were detected in soil and ground water near this suspected spill location in 1994 but not in upgradient ground water or soil (CH2M Hill, 1996). Other potential sources of TCE in ground water include Building 1059 (Fig. 1b), which has been used as a garage and motor pool, and dry wells reportedly connected to Building 1060 floor drains (CH2M Hill, 1994). In 1994, TCE, GRO and DRO ground-water contamination extended

northwest to the bank of the Chena River and covered approximately 1.5 hectares (3.8 acres).

All AI/SVE operations were conducted independently of this study. Details of system design and operation have been previously described in a remedial workplan and project progress reports (CH2M Hill, 1994, 1996, 1998). AI/SVE of DRO and GRO in ground water (approximately 25 m east of Building 1060) began in 1994. Injection wells were constructed of 0.05 m PVC pipe and were screened in the saturated zone between 8.5 and 9.1 m bgs (4.6 - 6.1 m below the water surface) in areas identified as having the greatest contaminant mass. SVE near Building 1060 began in July 1994. SVE wells near the TCE spill were shut down in October 1995 after SVE recovery lines were breached during other activities; SVE resumed the following spring. Air spargers at Building 1060 were not brought online until October 1996, one month after the first sampling of this study, because there was concern that high concentrations of petroleum hydrocarbons in soils would quickly saturate the granular activated carbon collection system. Operation of AI/SVE continued until November 1996 when frozen condensation blocked SVE lines. The entire system was restarted in June 1997. Air injection was shut down briefly in August 1997 to accommodate our sampling crew then operated continuously for the remainder of our study. Heat trace tape installed to prevent freezing condensation in SVE lines was maintained above 14 °C and appeared to increase temperatures in nearby ground water by several degrees (Hinzman et al., 2000). During the first year of operation, the radius of influence around air spargers was determined to be approximately 3 m, however, measured DO at wells 6386 and 6884 never exceeded 2 mg/L in our

samples. AI/SVE was not designed nor expected to remediate the very large ground-water contaminant plume located downgradient of the treatment area. Because ground water contamination extended well beyond the influence AI/SVE activity, we were able to examine microbiology and geochemistry associated with natural attenuation of TCE in both treated and untreated ground water.

The geologic and hydrologic characteristics of this site have been described previously (Nakanishi and Lilly, 1998). Interior Alaska is semi-arid, receiving an average of 0.28 m of precipitation annually, and regional aquifer recharge is primarily from Alaska Range snowmelt. Chena Alluvium sediments consist of sand and gravel mostly from glacial outwash (Nelson, 1978) derived from mafic (containing reduced iron and manganese) minerals from the Alaska Range with little oxidation due to glacial transport (Downey and Sinton, 1990). In the study area, depth to bedrock is >100 m below ground surface (bgs). Discontinuous permafrost is present throughout the region (Péwé et al., 1976) although permafrost was not encountered during drilling at this site; where absent, the aquifer is considered unconfined. Depth to ground water averages 6 m bgs although this can vary up to 3 m in response to seasonal fluctuations of Chena River stage. Hydraulic conductivity is approximately 122 m per day. Porosity varies due to the braided nature of silt, sand and gravel deposits and ranges between 0.25 and 0.5. The regional aquifer has a relatively flat horizontal gradient of about 0.001 $m \cdot m^{-1}$ (Nakanishi and Lilly, 1998) although significant variations in local gradients occur in response to changes in Chena River stage. Average linear ground-water velocity also varies considerably due to sediment heterogeneity and seasonal fluctuations in hydraulic

gradients. Reported average velocities have been as low as 12.2 $m \cdot yr^{-1}$ (CH2M Hill, 1994), and as high as 67 to 135 $m \cdot yr^{-1}$ (Nakanishi and Lilly, 1998). Given the very rapid migration of TCE in ground water at this site, it is likely that the latter estimates are closer to actual ground-water velocity.

In the study area, ground water generally flows northwest from the Tanana River towards the Chena River during most of the year (Fig. 1a) but as the Chena River rises dramatically in late April to early May due to snowmelt runoff and ice jams, ground water flow direction reverses and oxygenated surface water recharges the aquifer (Taras and Grant, 1995); the extent of surface-water influx, however, does not generally exceed about 3 m. Although water table rises that accompany flow reversals are attenuated with distance from the river, they can still be as much as 50% of river stage rise at a distance of 250 m from the bank. Late-summer rainfall typically results in one or more discharge peaks with corresponding ground-water flow reversals although these peaks generally are not as dramatic as those seen during spring breakup (Nakanishi and Lilly, 1998).

1.2.2. Methods

1.2.2.1. Well Construction and Purging

Detailed sampling, analysis and quality assurance procedures have been previously described (McCarthy et al., 1998). All monitoring wells were constructed of 0.05 m diameter PVC. Most had 0.76 m screens while a few water-table wells had 3.7 m screens. Well depths ranged between 6.1 and 18.3 m bgs. In addition to existing wells at the TCE source and near plume boundaries, three well clusters were installed in April

1997 (7315 - 7323, Fig. 1b). Each cluster consisted of 3 wells, individually screened at 6.1, 9.1, or 12.2 m bgs. Another monitoring well, 7331, was installed 1.5 m from the bank of the Chena River with multi-level sampling ports at 1.5 m increments to a depth of 12.3 m bgs. Ground water was sampled in fall and spring for two consecutive years. Before sampling, wells were purged with a peristaltic pump until at least three casing volumes of water had been removed and specific conductance, pH, DO, and temperature had stabilized. These parameters were measured with a multiprobe and a flow-through cell (Hydrolab Corp.).

1.2.2.2. Geochemical Sampling and Analysis

After purging, dissolved oxygen concentrations were measured colorimetrically (Hach, Co.). H_2 samples were collected using the bubble-strip method (Chapelle and McMahon, 1991) and analyzed at ambient temperatures by gas chromatography (GC) and an RGD2 reduced gas detector (Trace Analytical). Standards were prepared several times daily by diluting hydrogen (100 ppm; Scott Specialty Gases) in stoppered serum bottles containing UHP nitrogen at atmospheric pressure and results were regressed ($P \leq 0.05$). When collecting ground-water samples, equilibration was assumed when hydrogen concentrations measured in two samples collected at a 5-minute interval deviated < 5%. Dissolved hydrogen concentrations were calculated using the ideal gas law, the Henry's law constant (H_{H2}; Stumm and Morgan, 1981) and in situ ground-water temperatures. Ground-water samples for dissolved methane were collected in triplicate from a sampling bulb (Supelco, Inc.) with a gas tight syringe, filtered through a sterile 0.45 μm syringe

filter while injecting sample into sterile, O_2-free, stoppered serum vials. Samples were chilled (4 °C) until analysis by gas chromatography with flame ionization detection (GC/FID; Shimadzu) within 1 week. Methane concentrations were calculated as with hydrogen, using the Henry's law constant, H_{CH4}, (Stumm and Morgan, 1981) and previously described methods (McCarthy et al., 1998).

After purging, most ground-water samples were collected and shipped to the USGS National Water Quality Laboratory (NWQL; Denver, CO) where they were analyzed using previously published methods (Fishman et al., 1994). For these analyses, samples for sulfate were filtered through a 0.45 μm filter (Pall Gelman Laboratories) into polyethylene bottles, acidified with HNO_3 and chilled (4 °C) until analysis by ion chromatography. Samples for dissolved iron and manganese were filtered as before, acidified with HCl and chilled until analysis by inductively coupled plasma with mass spectroscopy (ICP/MS). Samples for ammonia-N, nitrate-N, nitrite-N, and orthophosphate were filtered as before, chilled, and analyzed colorimetrically. Chloride samples were chilled until analysis by ion chromatography. Total organic carbon (TOC) samples were collected into pre-cleaned amber glass bottles and chilled (4 °C) until analysis by standard methods (Fishman et al., 1994). Samples for volatile organics analyses were collected with Teflon® bailers (Voss Technologies), transferred to VOA septum vials, acidified with organic-free HCl and chilled (4 °C) until analysis by GC/MS.

Total iron was measured colorimetrically in the field on unfiltered samples using the FerroVer method (Hach, Co.) and quantities of suspended colloidal and/or particulate ferric iron were calculated by difference between total and dissolved iron. Samples for

total sulfide in unfiltered samples were analyzed on-site immediately after collection using the methylene blue method, equivalent to US EPA method 376.2 for wastewater (Hach, Co.); estimated detection limit is 2 μg/L.

1.2.2.3. Microbiological Sampling and Analysis

Samples were collected aseptically with sterile, Teflon® bailers, transferred to sterile polyethylene bottles, and chilled (4 °C) until analysis within 24 h of collection. Heterotrophic microorganisms in ground water were enumerated in triplicate using miniaturized, 6-tube most probable number (MPN) assays (Braddock and McCarthy, 1996) and 1/5 strength R2A medium (Atlas, 1993). Numbers of diesel-, gasoline-, and toluene-degrading microorganisms were measured using similar miniaturized MPN assays (Braddock and Catterall, 1999) but with Bushnell-Haas mineral salts medium (Atlas, 1993) with tetrazolium violet added as an indicator of aerobic respiration instead of R2A medium. Results are reported as MPN/mL. Relative numbers of methanotrophic bacteria were estimated by filtering known volumes (60 – 250 mL) of ground water through 0.45 μM filters (Millipore). Filters were placed onto sterile media pads that had been saturated with a minimal salts solution (Graham et al., 1992). Plates were incubated aerobically in a sealed vacuum jar (approximately 10 – 25% v/v methane/air) at ambient laboratory temperature for approximately 3 weeks. Headspace O_2 and CH_4 were intermittently replenished. Relative numbers are reported due to confluent growth on some plates (e.g., excessive growth prohibited enumeration of separate, distinct colonies).

1.3. Results

1.3.1. Hydrology and Geochemistry

Ground water in the study area is naturally anaerobic, with DO concentrations at most untreated wells < 0.05 mg/L. Surface-water influx did not appreciably aerate ground water, even at monitoring well 7331 which is adjacent to the riverbank. There, DO concentrations remained < 0.8 mg/L when measured during spring 1997 aquifer recharge (Wegner, 1998; Hinzman et al., in press). Dissolved Fe(II) concentrations were moderate and showed no trend in spatial distribution but were significantly greater in summer 1997 ($P < 0.05$; Fig 2a; Fig. 3a). Sulfate concentrations were moderately high and fluctuated considerably between samplings (Fig 2b; Fig 3b). Sulfides were present at low levels in many wells and concentrations were unexpectedly greatest in treated wells (6386 and 6884), even when air injectors were operating. Alkalinities were moderately high and fluctuated with time (Fig. 2c; Fig. 3c). Methane concentrations were low, < 100 μg/L at all wells (Fig. 2c; Fig. 3c). H_2 concentrations (Table 1.1) were generally within or below the range suggestive of iron reduction (0.1-0.8 nM; Lovely et al., 1994) although in April 1997, concentrations at some sampling points were greatly elevated as a result of recent well installation and therefore, not usable as geochemical indicators; concentrations later stabilized at much lower levels. Similar results have been reported previously (Bjerg et al., 1997).

Approximately 27 kg of TCE and partially dechlorinated transformation intermediates were reportedly recovered via active treatment in 1997 (CH2M Hill, 1998). However, ground water contaminant concentrations were still substantial when measured

in 1997 and 1998, suggesting that the reported surface spill of TCE near Building 1060 was likely not the only source of TCE contamination at this site.

At treated wells 6386 and 6884, TCE concentrations had decreased substantially before AI/SVE began (Fig. 4a, b) although concentrations of *cis*-1,2-DCE increased after air injection began; trans-DCE was generally not detected. At untreated wells 6385 and 6885, contaminant concentrations decreased substantially and plume boundaries stabilized prior to active treatment at the spill site (Fig. 4c, d). At 6385, *cis*- and *trans*-DCE were present in near equal quantities. At these untreated wells, TCE loss exhibited first-order "decay," with rate constants of 1.2 and 1.6 $year^{-1}$ (r^2 = 0.997 and 0.994), respectively. Estimated half-lives for TCE losses at untreated wells were between 5 and 7 months, which are relatively low, likely due to fairly rapid ground-water velocities (Sorenson et al., 2000), dilution, and/or low TCE concentrations. Vinyl chloride and BTEX compounds were not detected in any samples (Appendix A).

Concentrations of total organic carbon (TOC) were generally low (4.9 mg/L ± 1.19; mean ± standard error). In September 1996, TOC at 6386 was 18.0 mg/L, which is greater than TOC measured at other wells but significantly lower than previously reported concentrations of DRO and GRO, suggesting that these contaminants were being naturally attenuated. Nutrient concentrations also were low but were generally sufficient to support microbial growth. Nitrogen (as ammonia, nitrate or nitrate) and phosphorus concentrations ranged from < 0.01 to 1.87 mg/L, with most concentrations above the lower detection limits for all parameters measured. Nitrogen was generally present as ammonia and therefore, not available as an electron acceptor (Hinzman et al., 2000).

1.3.2. Microbiology

In April 1997, numbers of aerobic heterotrophic microorganisms ranged between approximately 10^3 and 5×10^6 cells/mL (Fig. 5a). At that time, air injectors had been off for about 6 months. In April 1998, after a year of near-continual air injection, cell numbers at treated wells increased to approximately 8×10^9 cells/mL while numbers at untreated wells were generally unchanged (Fig. 5b). Numbers of methanotrophic bacteria were measured in April 1998 at treated wells and an untreated well, 7319. Numbers were greatest in treated ground water and were not detected at 7319 (Table 2.2). Most probable numbers of aerobic gasoline, diesel, and toluene-degrading microorganisms were about $10^3 - 10^4$ MPN/mL at all wells and did not very spatially or between treated and untreated wells (results not shown).

1.4. Discussion

Since TCE transformation processes are highly dependent on prevailing redox conditions, a careful assessment of in situ TEAPs was important to determine which transformation reactions could potentially occur. At this subarctic site, ground water is naturally anaerobic, and potential electron acceptors (i.e., ferric iron, sulfate, and carbonate) show substantial temporal fluctuation (Hinzman et al., 2000). In addition, concentrations of the reduced products of terminal metabolism fluctuate normally (i.e., ferrous iron), are low (i.e., sulfide), or may be present as a result of diffusion from other sources (i.e., methane). Combined, these factors make the distribution of electron acceptors and end products unreliable indicators of predominant TEAPs at this site.

Hydrogen measurements were more useful. With the notable exception of spring 1997, when sampling occurred shortly after well installation and hydrogen concentrations were anomalously high, hydrogen concentrations were generally suggestive of iron reduction; some measurements were within the range predicted for manganese reduction. Substantial quantities of suspended ferric iron were present in most samples and, although speculative, more may have been present as coatings on individual aquifer grains since ferric hydroxides tend to aggregate and adhere to surfaces after precipitation (Cerundolo et al., 1988). Collectively, iron and hydrogen data suggest that iron reduction was the predominant TEAP at this site. However, there is also evidence that some sulfate reduction may have occurred as the presence of dissolved sulfide in ground water is indicative of local production (Christensen et al., 1994). Given the heterogeneous nature of this aquifer, it may be that sulfate reduction occurred in pockets of stagnant pore water where hydrogen concentrations were higher. The same could be true for methanogenesis but it is important to note that methane appears to be common in Fairbanks-area ground water (Richmond and Braddock, 2000; Richmond et al., submitted) and may simply reflect diffusion from underlying peat or permafrost, present throughout the region (Péwé et al., 1976; Kvenvolden and Lorenson, 1993).

Ground-water geochemistry and microbiology near AI wells varied in response to aeration. DO concentrations at monitoring wells 6386 and 6884 were only 1.4 and 1.9 mg/L, respectively, in 1998 when AI was operating; DO concentrations near other injection points not included in this study ranged between 7.2 – 12.5 mg/L (CH2M Hill, 1996). In spite of aeration, evidence of sulfate reduction, a strictly anaerobic process,

was unexpectedly observed at treated wells 6386 and 6884, where sulfide concentrations were highest at all samplings (Fig. 3b). At these wells in particular, purge water smelled strongly of hydrogen sulfide and contained a black precipitate, presumably ferrous sulfide. Such convincing evidence of anaerobic conditions near treated wells suggests biofouling due to greatly elevated numbers of aerobic heterotrophic microorganisms (Fig. 5a, b) or plugging of aquifer sediments by precipitated iron hydroxides as a result of oxygenation. Plugging may have led to the formation of highly anaerobic, localized microenvironments in stagnant pore water. If true, these localized anaerobic conditions would enable reductive dechlorination of TCE by sulfate-reducing bacteria. Anaerobic reductive dechlorination in highly localized microenvironments is a likely mechanism by which, at monitoring well 6884, *cis*-DCE concentrations approximately doubled while TCE concentrations decreased after sparging began (Fig. 4a, b). In addition to increased numbers of heterotrophic microorganisms, relative numbers of methanotrophic bacteria were much higher in the treatment area than at an untreated reference well (Table 1.1). Methanotrophs have been shown to aerobically cometabolize a variety of chlorinated aliphatics (Vogel and McCarty, 1987 and references cited therein) and, although somewhat speculative, it is possible that methanotrophic activity contributed to contaminant loss in aerobic ground water near AI wells.

Beyond the area influenced by air injection, there is evidence that natural attenuation processes occurred. At representative untreated monitoring well 6885, contaminant concentrations decreased and plume boundaries stabilized before AI/SVE began (Fig. 4d). Since TCE and DCE concentrations decreased simultaneously at this

sampling point, it seems likely that dilution and dispersion were the predominant attenuation mechanisms at the periphery of the plume; DCE may have simply been transported from the upgradient portion of the contaminant plume. Relative proportions of DCE isomers varied among treated and untreated ground-water samples. In treated ground water, *cis*-DCE was present whereas the trans isomer was not (Fig. 4a, b). At untreated well 6385, approximately equal proportions of both DCE isomers were present (Fig. 4c). These data suggest that reductive dechlorination occurred and that the mechanisms were different from those occurring in treated ground water. However, the precise mechanism by which reductive dechlorination may have occurred in untreated ground water is unclear; perhaps different dechlorinating organisms were present in treated and untreated ground water or abiotic reactions occurred in untreated ground water. It seems probable, however, that any dechlorination processes occurring in untreated ground water were different from those occurring in treated ground water.

Few studies have addressed TCE transformation processes in subarctic ground water. This study examined differences in microbiology and geochemistry associated with TCE transformation between treated and untreated subarctic ground water to determine which transformation processes might have occurred. Since ground water at this site was only weakly reducing and reductive dechlorination appeared to stall at DCE, it is unlikely that bioattenuation represented a significant component of contaminant removal. In the absence of active treatment, advection and dispersion were likely the primary attenuation mechanisms. However, biological transformation processes did occur. Elevated concentrations of sulfide near air injectors indicated active sulfate

reduction, which probably occurred in localized, anaerobic microenvironments and provided an environment favorable for reductive dechlorination. Increased concentrations of *cis*-DCE near treated wells suggested biological reductive dechlorination might have occurred within the stagnant pore water of these microenvironments. In the treated, aerobic ground water surrounding these stagnant zones, numbers of methanotrophic bacteria were greatest. These bacteria may have aerobically co-metabolized TCE and DCEs. Beyond the influence of active treatment, near equal concentrations of *cis*- and *trans*-DCE were observed, suggesting different dechlorination mechanisms than those occurring near treated wells.

Although there was evidence that biological and perhaps chemical reactions associated with TCE transformation occurred at this subarctic site, it is important to note that contaminant loss was largely attributable to dilution and dispersion. Increased human activity in northern latitudes increases the possibility of larger and more frequent releases of environmental contaminants thereby posing a potential threat to local water supplies and wildlife. Continued research into the mechanisms and rates of contaminant transformation in cold environments is necessary before natural attenuation can be considered a viable treatment option at other subarctic sites.

1.5. Acknowledgments

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1.6. Literature Cited

Atlas, R.M., 1993. *Handbook of Microbiological Media.* CRC Press, Boca Raton, FL. pp. 1079.

Bjerg, P.L., Jakobsen, R., Bay, H., Rasmussen, M., Albrechtsen, H.-J., Christensen, T.H., 1997. Effects of sampling well construction on H_2 measurements made for characterization of redox conditions in a contaminated aquifer. Environ. Sci. Technol. 31, 3029-3031.

Braddock, J.F., McCarthy, K.A., 1996. Hydrologic and microbiological factors affecting persistence and migration of petroleum hydrocarbons spilled in a continuous-permafrost region. Environ. Sci. Technol. 30, 2626-2633.

Braddock, J.F. and P.H. Catterall. 1999. A simple method for enumerating gasoline- and diesel-degrading microorganisms. Bioremed. Jour. 3, 81-84.

Bradley, P.M., Chapelle, F.H., 1996. Anaerobic mineralization of vinyl chloride in Fe(III)-reducing aquifer sediments. Environ. Sci. Technol. 30, 2084-2086.

Bradley, P.M., Chapelle, F.H., 1997. Kinetics of DCE and VC mineralization under methanogenic and Fe(III)-reducing conditions. Environ. Sci. Technol. 31, 2692-2696.

Bradley, P.M., Landmeyer, J.E., Dinicola, R.S., 1998. Anaerobic oxidation of [1,2- ^{14}C] dichloroethene under Mn(IV)-reducing conditions. Appl. Environ. Microbiol. 64, 1560-1562.

Cerundolo, D.L., Coons, S.F., Gibson, E.D., Loreti, C.P., 1988. Chapter 6, *Matrix Elements and Ligands.* In: Bodek, I., Lyman, W.J., Reehl, W.F., Rosenblatt, D.H., 1988. *Environmental Inorganic Chemistry.* Pergamon Press, New York.

CH2M Hill, 1994. Building 1060 treatability study plan, delivery order 10, Fort Wainwright, Alaska.

CH2M Hill, 1996. Building 1060 treatability study annual report, year one (July 1994 to December 1995).

CH2M Hill, 1998. Building 1060 treatability study annual report, year three (January 1997 to December 1997).

Chapelle, F.H., McMahon, P.B., 1991. Geochemistry of dissolved inorganic carbon in a Coastal Plain aquifer. 1. Sulfate from confining beds as an oxidant in microbial CO_2 production. J. Hydrol. 127, 85-108.

Christensen, T.H., Kjeldsen, P., Albrechtsen, H.-J., Heron, G., Nielsen, P.H., Bjerg, P.L., Holm, P.E., 1994. Attenuation of landfill leachate pollutants in aquifers. Crit. Rev. Environ. Sci. Technol. 24, 119-202.

Davis, J.W., Carpenter, C.L., 1990. Aerobic biodegradation of vinyl chloride in groundwater samples. Appl. Environ. Microbiol. 56, 3878-3880.

Downey, J.S. and Sinton, P.O., 1990. Geohydrology and ground-water geochemistry at a sub-arctic landfill, Fairbanks, Alaska. U.S. Geological Survey Water-Resources Investigations Report 90-4022.

Enzien, M.V., Picardal, F., Hazen, T.C., Arnold, R.G., Fliermans, C.B., 1994. Reductive dechlorination of trichloroethylene and tetrachloroethylene under aerobic conditions in a sediment column. Appl. Environ. Microbiol. 60, 2200-2204.

Federal Register, 1989. Environmental Protection Agency, National Primary and Secondary Drinking Water Regulations 21, pp. 22062-22160.

Fishman, M.J., Raese, J.W., Gerlitz, C.N., Husband, R.A., 1994. U.S. Geological Survey approved inorganic and organic methods for the analysis of water and fluvial sediment, 1954-1994: U.S. Geological Survey Open-File Report 94-351.

Graham, D.W., Korich, D.G., LeBlanc, R.P., Sinclair, N.A., Arnold, R.G., 1992. Applications of a colorimetric plate assay for soluble methane monooxygenase activity. Appl. Env. Microbiol. 58, 2231-2236.

Hinzman, L.D., Lilly, M.R., Braddock, J.F., McCarthy, K.A., Richmond S.A., Wegner, M.A., 2000. Natural attenuation of chlorinated-hydrocarbon contamination at Fort Wainwright, Alaska: A hydrogeochemical and microbiological investigation. University of Alaska Fairbanks, Institute for Northern Engineering/Water and Environmental Research Center Report 00.02.

Hinzman, L. D., Wegner, M.A., Lilly, M.R. Hydrologic investigations of ground-water and surface-water interactions in subarctic Alaska. Nordic Hydrol. In Press.

Kvenvolden, K.A., Lorenson, T.D, 1993. Methane in permafrost—preliminary results from coring at Fairbanks, Alaska. Chemosphere 26, 609-616.

Löffler, F.E., Tiedje, J.M., Sanford, R.A., 1999. Fraction of electrons consumed in electron acceptor reduction and hydrogen thresholds as indicators of halorespiratory physiology. Appl. Environ. Microbiol. 65, 4049-4056.

Lovely, D.R., Chapelle, F.H., and Woodward, J.C., 1994. Use of dissolved H_2 concentrations to determine distribution of microbially catalyzed redox reactions in anoxic ground water. Environ. Sci. Technol. 28:1205-1210.

McCarthy, K.A., Lilly, M.R., Braddock, J.F., Hinzman, L.D., 1998. Natural attenuation of chlorinated-hydrocarbon contamination at Fort Wainwright, Alaska: A hydrogeochemical and microbiological investigation workplan. U.S. Geological Survey Open-File Report 98-198.

Nakanishi, A.S., Lilly, M.R., 1998. Estimate of aquifer properties by numerically simulating ground-water/surface-water interactions, Fort Wainwright, Alaska. U.S. Geological Survey Water-Resources Investigations Report 98-4088.

National Research Council (NRC), 2000. Natural Attenuation for Groundwater Remediation/Committee on Intrinsic Remediation, Water Science and Technology Board [and] Board on Radioactive Waste Management, Commission on Geosciences, Environment, and Resources. National Academy Press, Wash., D.C. 274 pp.

Nelson, G.L., 1978. Hydrologic information for land-use planning, Fairbanks vicinity, Alaska. U.S. Geological Survey Open-File Report 79-959.

Péwé, T.L., Bell, J.W., Forbes, R.B., Weber, F.R., 1976. Geologic map of the Fairbanks D-2 SW quadrangle, Alaska. U.S. Geological Survey Miscellaneous Investigations Series Map I-829-A, scale, 1:24,000, 1 sheet.

Phelps, T.J., Niedzielski, J.J., Malachowsky, K.J., Schram, R.M., Herbes, S.E., White, D.C., 1991. Aerobic mineralization of vinyl chloride by a bacterium of the order Actinomycetales. Environ. Sci. Technol. 25, 1461-1465.

Richmond, S.A., Braddock, J.F., 2000. Geochemical characterization of anaerobic ground water in subarctic Alaska. Proceedings of the American Water Research Association Conference: Water Resources in Extreme Environments. Middleburg, Virginia, TPS-99-4, pp. 141-145.

Richmond, S.A., Lindstrom, J.E., Braddock, J.F. Assessment of natural attenuation of chlorinated aliphatics and BTEX in subarctic ground water. Submitted.

Sorenson, K.S., Jr., Peterson, L.N., Hinchee, R.E., Ely, R.L., 2000. An evaluation of aerobic trichloroethene attenuation using first-order rate estimation. Bioremediation J. 4, 337-357.

Stumm W. and Morgan, J.J, 1981. *Aquatic Chemistry*, 2nd Ed., John Wiley and Sons, Inc.: New York. 780 pp.

Taras, B.D., Grant, S.A., 1995. Continuous determination of ground water flow direction and gradient at selected sites of CERCLA concern, Fort Wainwright, Alaska, second year, first interim report. U.S. Army Cold Regions Research and Engineering. Laboratory Contract Report No.28.

Vogel, T.M., McCarty, P.L., 1985. Biotransformation of tetrachloroethylene to trichloroethylene, dichloroethylene, vinyl chloride, and carbon dioxide under methanogenic conditions. Appl. Environ. Microbiol. 49, 1080-1083.

Vogel, T.M., Criddle, C.S., McCarty, P.L., 1987. Transformations of halogenated aliphatic compounds. Environ. Sci. Technol. 21, 722-736.

Wegner, M.A., 1998. Transient ground water and surface-water interactions at Fort Wainwright, Alaska. M.S. Thesis, University of Alaska Fairbanks, Fairbanks, Alaska, pp. 75.

Table 1.1. Dissolved-hydrogen concentrations in ground water at Fort Wainwright, Alaska, September 1996 to April 1998. All concentrations nM.

Well	September 1996	April 1997[a]	August 1997[b]	April 1998
6385	<0.05	0.15	--	0.10
6386	--	0.10	--	0.09
6884	0.2	0.10	0.30	0.11
6885	0.9	--	--	--
7315	--	6.06	--	0.10
7316	--	3.4	--	0.15
7317	--	0.67	--	0.19
7318	--	0.68	--	0.12
7319	--	< 0.1	--	0.09
7320	--	629	--	0.11
7321	--	0.79	--	0.06
7322	--	6.4	--	0.16
7323	--	1.6	--	0.09

[a]Monitoring wells 7315-7323 installed in April 1997; hydrogen concentrations anomalously high at some wells due to recent installation. [b]Hydrogen not measured at most wells in August 1997 due to equipment failure. --No data.

Table 2.2. Relative numbers of methanotrophic bacteria in ground water, Fort Wainwright, Alaska, April 1998. * indicates wells influenced by air injection.[a]

Monitoring Well	Relative Growth
FWM6884*	++
FWM6386*	+
FWM7319	-

[a] ++, Confluent growth; +, moderate growth; -, no growth

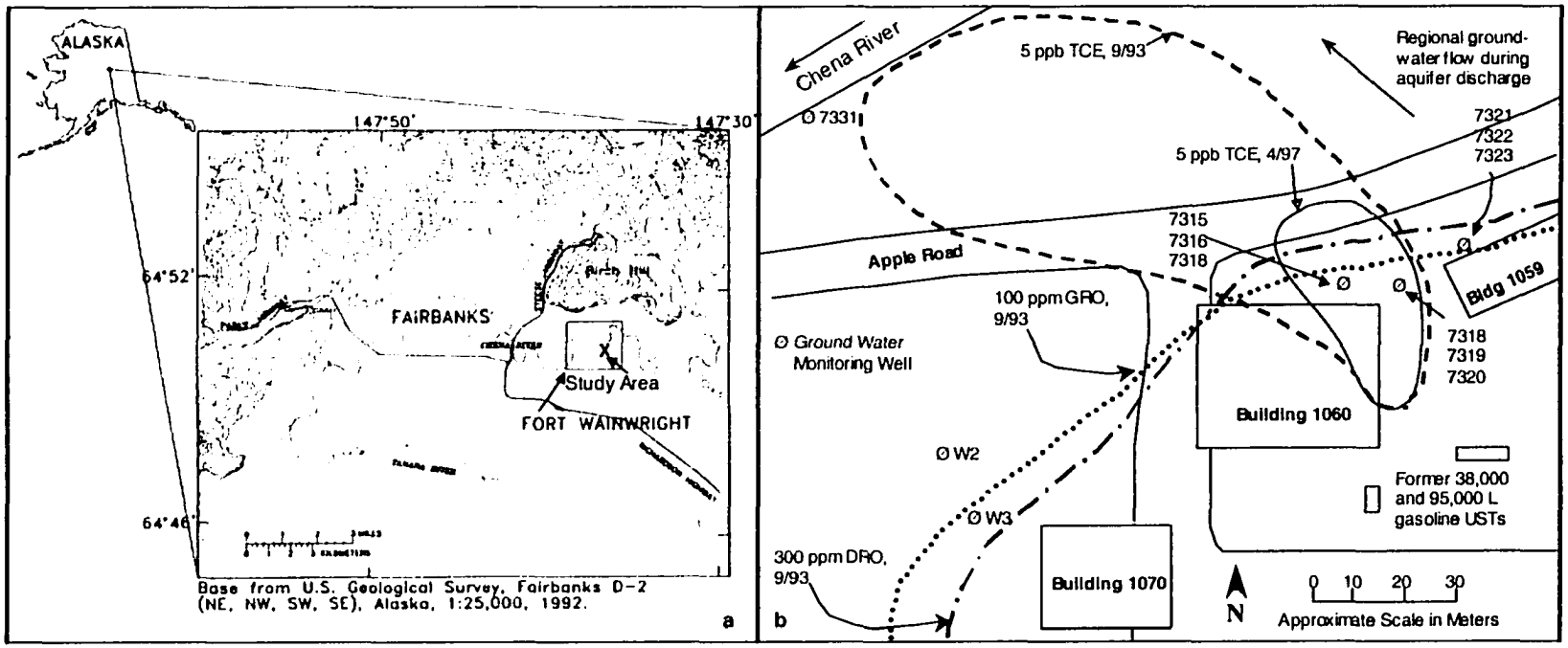

Figure 1.1. Location of study area (a) and Building 1060 and monitoring wells located on Fort Wainwright, Alaska (b).

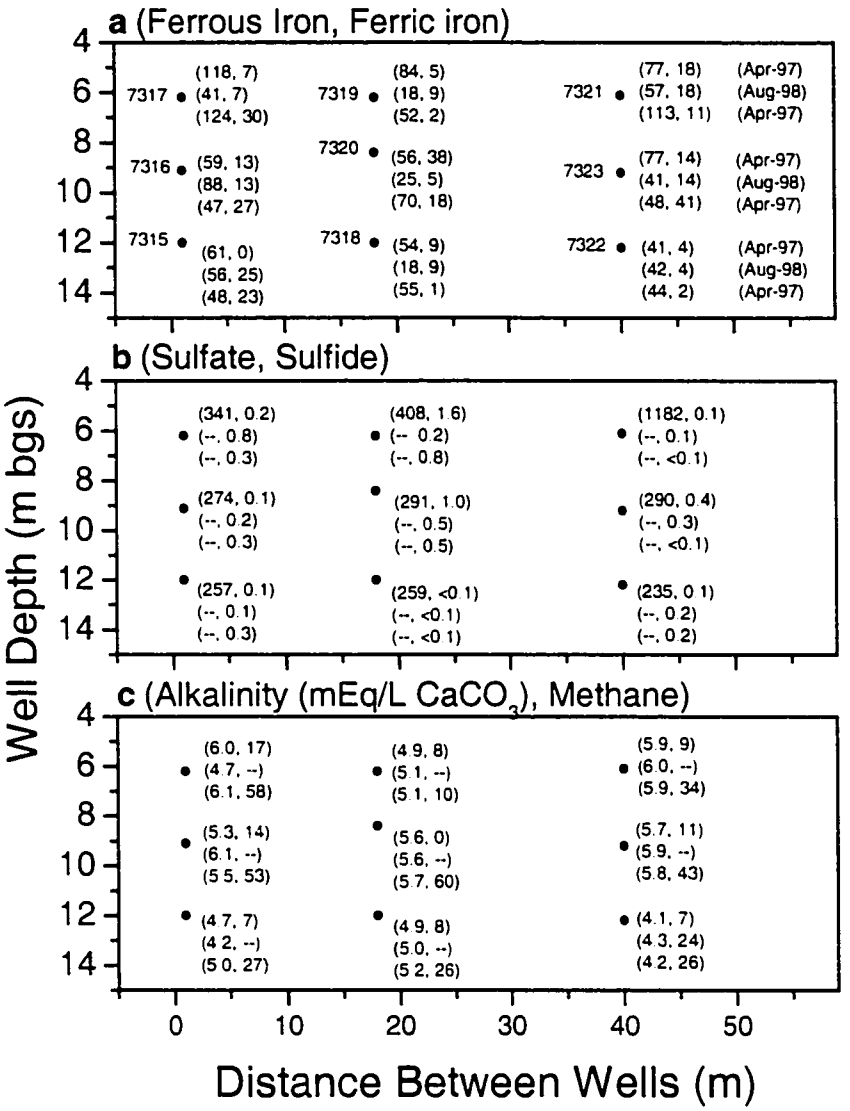

Figure 1.2. Ground-water geochemistry at Fort Wainwright, Alaska, 1997 – 1998, within a horizontal cross-section of TCE the plume at monitoring wells 7317-7323 (well locations identified in panel a). • indicates monitoring well. Each well was sampled three times, as indicated in panel a: April 1997 (top), August 1997 (middle), and April 1998 (bottom). Ferrous, ferric iron (a; ferric iron present as colloidal and/or suspended solids in unfiltered samples); Sulfate, sulfide (b); Alkalinity (mEq/L $CaCO_3$), methane (c). All units in μM unless otherwise noted. -- indicates no data.

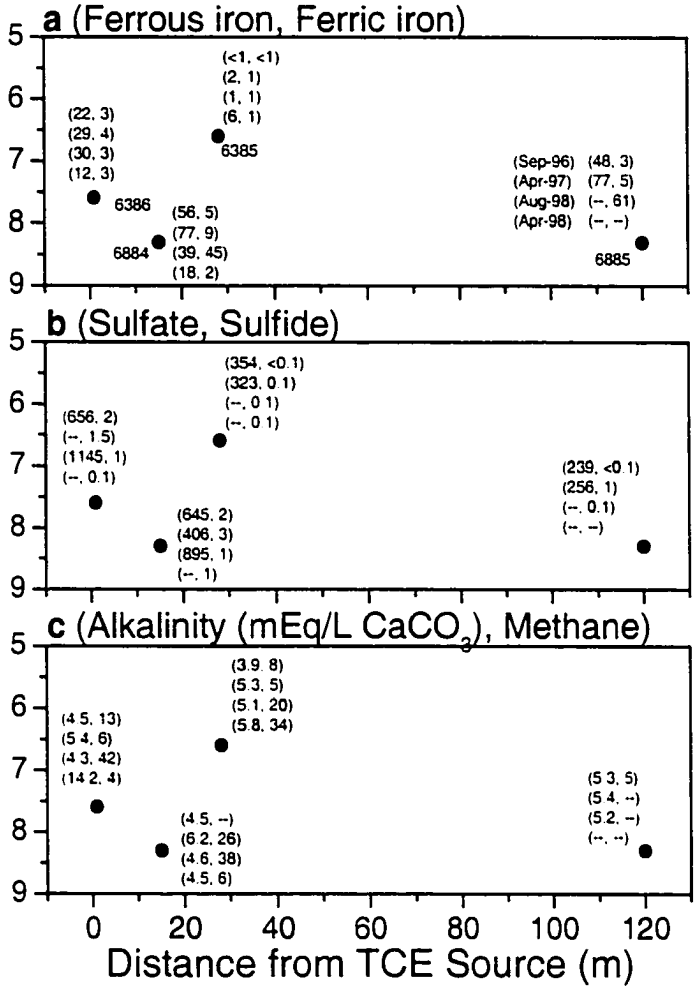

Figure 1. 3. Ground-water geochemistry at Fort Wainwright, Alaska, 1996 – 1998, along a longitudinal transect of the TCE ground-water plume at monitoring wells 6386, 6884, 6385, 6885, and 7331 (well locations indicated on panel a). • indicates monitoring well. Most wells were sampled four times, as indicated in panel a: September 1996 (top), April 1997 (mid-upper), August 1997 (mid-lower), and April 1998 (bottom). Ferrous, ferric iron (a; ferric iron present as colloidal and/or suspended solids and unfiltered samples); Sulfate, sulfide (b); Alkalinity (mEq/L $CaCO_3$), methane (c). All units in μM unless otherwise noted.

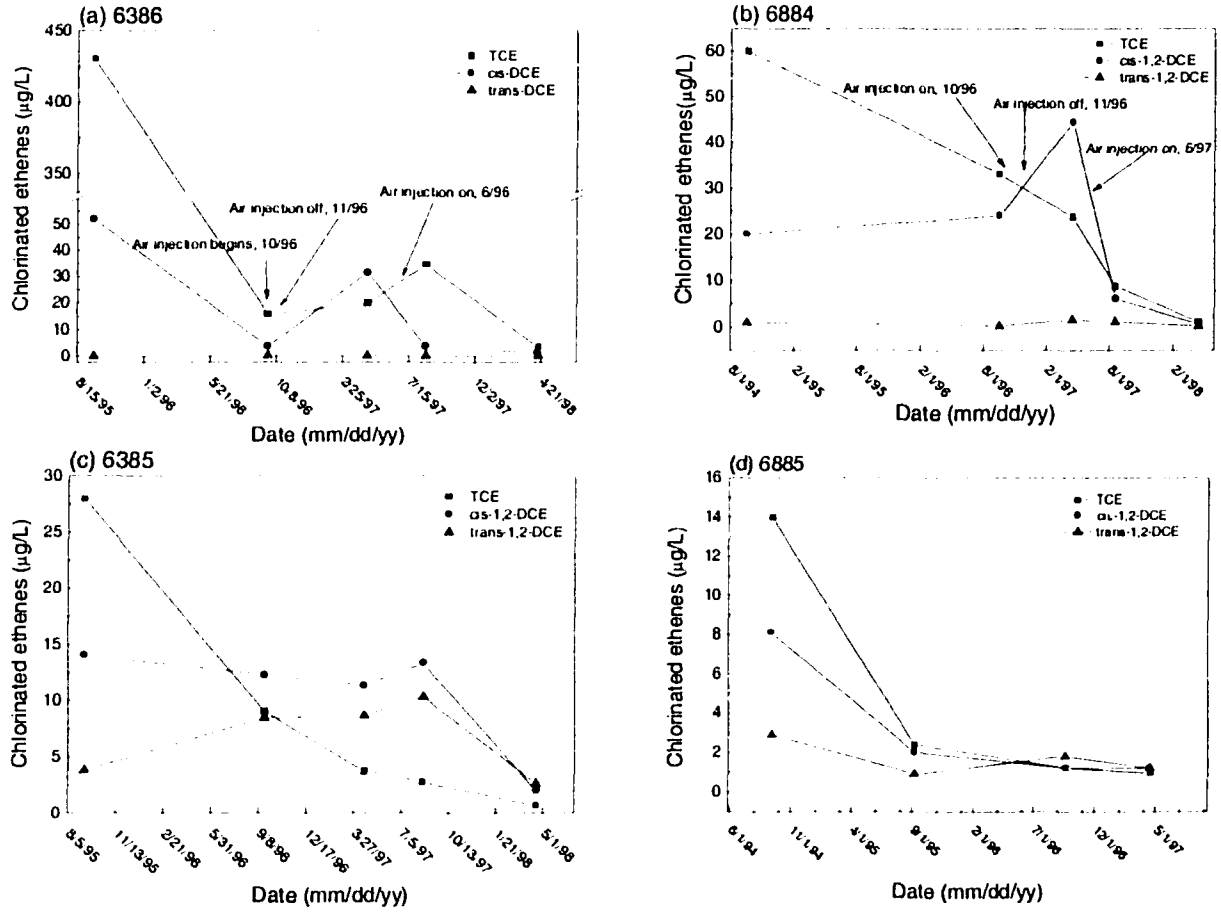

Figure 1.4. Concentrations of chlorinated ethenes at treated wells 6884 (a) and 6386 (b) located near the TCE source and at representative untreated wells 6385 (c) and 6885 (d) located beyond the influence of air injection. ■ Trichloroethene (TCE); ● *cis*-dichloroethene (*cis*-DCE); ▲ *trans*-dichloroethene (*trans*-DCE). Arrows indicate approximate start and stop dates of air injection. Note axis break on Fig. 4b.

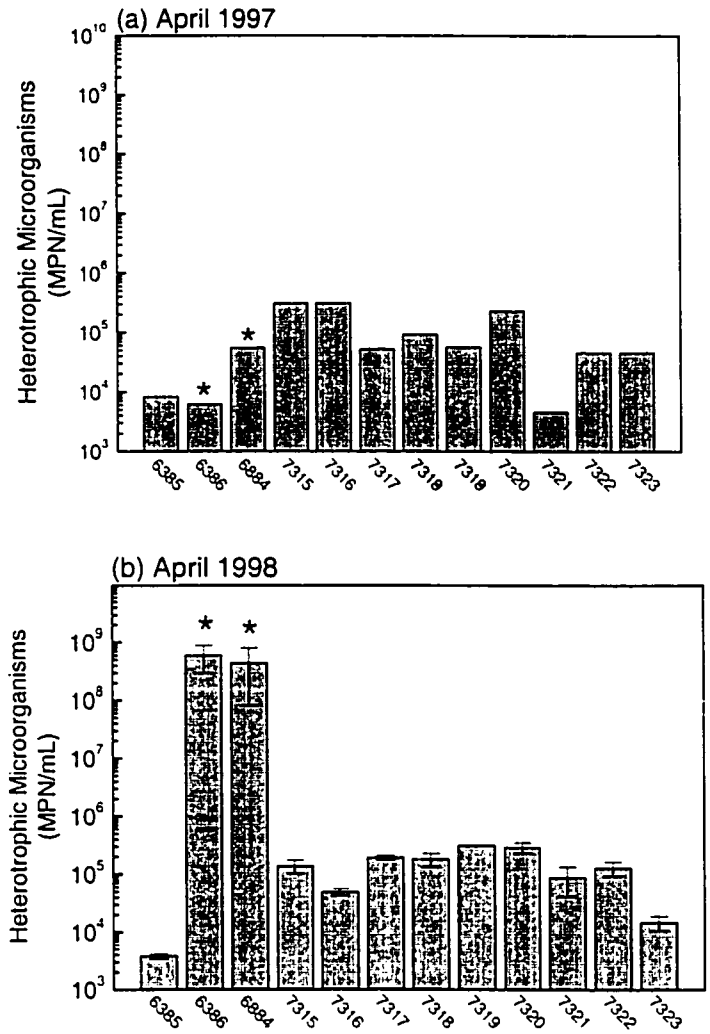

Figure 1.5. Most probable numbers (MPN) of aerobic heterotrophic microorganisms in ground water at Building 1060, April 1997 (a) and April 1998 (b). * wells influenced by air injection. Air injection began in October 1996 and continued intermittently through April 1998. Error bars represent standard errors about the mean of triplicate samples.

CHAPTER 2

Assessment of Natural Attenuation of Chlorinated Aliphatics and BTEX in Subarctic Ground Water[2]

Abstract

We examined biogeochemistry and microbiology associated with natural attenuation of low concentrations of trichloroethene (TCE), trichloroethane (TCA), and benzene, ethyl benzene, toluene and xylenes (BTEX) in cold (ca. 4 °C) ground water. Hydrogen concentrations at sampled wells were between 0.11 and 2.05 nM, with most wells < 0.8 nM, suggesting that iron reduction was the predominant terminal electron accepting process (TEAP). However, aquifer sediments are composed of mafic (containing reduced iron and manganese) minerals and particulate ferric iron concentrations were low, generally ≤ 0.1 mg/L. Sulfate concentrations were substantial (ca. 21 mg/L) and dissolved sulfide at most wells suggested active sulfate reduction. Calculated in situ Gibbs free energies for iron and sulfate reduction were energetically favorable at most wells sampled. Although methane was present in most samples (< 20 - 890 μg/L), methanogenesis from H_2/CO_2 was energetically feasible at only one well; measured methane may have diffused from permafrost or peat. Anaerobic glutamate mineralization potentials were significantly greater at 25 °C than 10 °C ($P < 0.05$). The

[2] Richmond, S.A., Lindstrom, J.E., Braddock, J.F. Assessment of natural attenuation of chlorinated aliphatics and BTEX in subarctic ground water. Submitted to *Environmental Science and Technology*.

presence of less chlorinated intermediates of TCE and TCA degradation suggested that biological reductive dechlorination occurred, although proportions of these intermediates relative to parent compounds remained stable after preliminary sampling. Vinyl chloride, ethene, and ethane were not detected. By September 2000, BTEX and chlorinated solvent concentrations were within drinking water standards in most samples. However, low rates of microbial activity, incomplete degradation of chlorinated solvents and persistence of contaminants imply that biologically mediated mechanisms did not likely represent an important contribution to natural attenuation of contaminants at this site, where dilution appeared to be the primary attenuation mechanism.

Keywords: Subarctic; Chlorinated solvents; BTEX; Redox; Hydrogen; Microbiology

2.1. Introduction

Monitored natural attenuation has become an increasingly attractive treatment strategy for remediation of contaminated ground water and soils because it is generally less expensive and, in some cases, more practical than engineered cleanup solutions. As of 1997, this approach had been implemented at tens of thousands of contaminated sites in the U.S. (U.S. EPA, 1997), either as the only treatment strategy or as a supplement to engineered solutions. The effectiveness of bioattenuation has been demonstrated at many sites, primarily those contaminated with high concentrations of gasoline or other petroleum fuels and located in more temperate climates. However, because the success of natural attenuation is highly dependent on the contaminants involved and on site-specific

microbiology, geochemistry, hydrology and other physical factors, its applicability at all contaminated sites is questionable (National Research Council (NRC), 2000).

It has been well documented that microbial mineralization and transformation of the gasoline components benzene, toluene, ethylbenzene, and xylenes (BTEX) occur readily under aerobic and, to a lesser extent, anaerobic conditions. Numerous studies have demonstrated that these compounds can be degraded by denitrifying, iron- and sulfate reducing, and fermentative microorganisms (Beller et al., 1992; Evans et al., 1991a, b; Lovely, 1997; Vogel and Grbić-Galić, 1986). Conversely, microbial transformation of chlorinated solvents such as trichloroethene (TCE) and trichloroethane (TCA) occurs only under a limited range of environmental conditions and their susceptibility to mineralization is generally low (NRC, 2000). Complete mineralization of TCE and TCA via reductive dechlorination generally requires highly reducing conditions and a proportionally large source of readily available electron donor. Without these conditions, dechlorination is oftentimes incomplete and may result in the accumulation of vinyl chloride, a known carcinogen (NRC, 2000). The conditions required for aerobic cometabolic transformations of chlorinated solvents (e.g., ample oxygen and primary carbon source—methane, toluene, or phenol) do not frequently occur. If the carbon source is present in quantities sufficient to support cometabolism, oxygen may be quickly depleted during degradation of the primary carbon source. In addition to these biologically mediated reactions, abiotic chemical transformations have been reported, notably the hydrolysis of TCA by water and reductive dechlorination of TCE by Fe (II) that is sorbed to solid materials within the aquifer (NRC, 2000). However, abiotic

reactions are typically quite slow (Vogel et al., 1987 and references cited therein). Discerning which, if any, transformation reactions may occur at a given site can be extremely difficult; it is therefore essential that a careful and thorough evaluation of ground water geochemistry, hydrology and microbiology be completed before natural attenuation is chosen as a viable treatment strategy at sites contaminated with chlorinated aliphatics.

Currently accepted protocols for assessing the feasibility of natural attenuation have been developed using data primarily collected from highly contaminated sites in temperate climates; their applicability to cold or very dilute systems is unclear. This paper addresses some of the difficulties encountered when assessing the feasibility of natural attenuation of BTEX, TCE and TCA in a subarctic aquifer. The combined effects of aquifer geochemistry, low contaminant concentrations, low levels of microbial activity and very cold temperatures made it unlikely that intrinsic bioremediation was a significant mechanism of contaminant removal at this site.

2.2. Materials and methods

2.2.1. Field Site

Six Mile Village, near Fairbanks, Alaska, is located about 3 km north of the Tanana River within the Tanana-Chena floodplain (Figure 1). Alluvial sediments are primarily sand and gravel from glacial outwash from the Alaska Range (Nelson, 1978). In the study area, depth to bedrock has not been conclusively determined although in a

nearby area, a thickness of ca. 180 m was reported (Nelson, 1978). Discontinuous permafrost is present throughout the region (Péwé et al., 1976) and permafrost lenses were encountered during drilling at this site. However, where permafrost is absent, the aquifer is considered unconfined. The alluvial plain is flat and depth to ground water is between < 0.3 to 5.0 m below ground surface (bgs) (Krumhardt, 1982). Interior Alaska is semi-arid, receiving an average of 0.28 m of precipitation annually, and regional aquifer recharge is primarily from Alaska Range snowmelt carried by the Tanana River. Seasonal fluctuations in ground water levels at the study site reflect changes in Tanana River stage and range between < 0.3 and 1.0 m, averaging about 0.6 m. These water-level fluctuations are most pronounced during spring thaw and are attenuated with distance from the river (Nelson, 1978). Aquifer porosity is approximately 25 - 40 percent (Nakanishi and Lilly, 1998). Regionally, horizontal hydraulic conductivity is estimated to be approximately 120 m day^{-1} (Nakanishi and Lilly, 1998) although hydraulic conductivity measured north of Six Mile Village was estimated to be approximately 8 m day^{-1} (Shannon &Wilson, 1994). Additional tracer tests performed at Six Mile Village in 1997 revealed a ground water velocity of approximately 1 m·day^{-1} (Shannon & Wilson, 1998) suggesting that hydraulic conductivity at the study site is actually closer to the U.S. Geological Survey estimate. However, ground water velocity within different portions of the aquifer must vary due to the heterogeneous nature of its braided deposits of silt, sand, gravel and cobbles. Regionally, the ground water flow direction is about N10°W to N15°W and the hydraulic gradient is 1.23 mm per m (Glass et al., 1996) although this varies locally and seasonally.

TCE, TCA, and intermediate degradation products of these compounds were discovered in ground water during several studies conducted between 1994 and 1996 and BTEX were detected in ground water as early as 1989. The precise locations, volumes, and release dates of these contaminants are mostly unknown although one BTEX source was serendipitously located during drilling for monitoring well installation in the downgradient portion of the BTEX contaminant plume. Contaminated soil at that location was excavated and removed from the site. It is not clear whether one continuous or two distinctly separate TCE contaminant plumes exist at the study site (Fig. 1) but the estimated area affected by contamination exceeds 20 hectares (50 acres) and encompasses two residential neighborhoods that relied entirely upon the ground water within the contaminant plume as a drinking water source. All geochemical data (inorganic and organic) collected between 1994 and 2000 are presented in a project report prepared for the Alaska Department of Environmental Conservation (Shannon & Wilson, 2000).

2.2.2. Well construction

All monitoring wells were constructed of 0.05 m diameter PVC. Most wells had 0.8 - 1.5 m screens while a few water-table wells had 3.7 m screens. Well depths ranged between 2 and 21 m below ground surface (bgs). Before sampling, wells were purged with a peristaltic pump until at least three casing volumes of water had been removed and specific conductance, pH, DO, oxidation reduction potential (ORP) and temperature stabilized. These parameters were measured with a multiprobe and a flow-through cell

(Yellow Springs Instruments). Because sampling points were spatially separated by considerable distance and/or were pumped at a low flow rate (< 1 L/min), pumping during purging and sampling could not cause significant mixing of ground water.

2.2.3. Inorganic and Organic Analyses

Ground water was sampled in the summers between 1994 and 2000. More frequent sampling is very difficult or impossible due to extreme weather conditions at other times of the year. Analyses for iron, sulfur and nitrogen were carried out with commercially available colorimetric reagents (Hach, Co.) and were performed on-site immediately upon collection. Dissolved ferrous iron and dissolved sulfide were measured in filtered (0.45 μm) samples; total recoverable iron and total sulfide were measured in unfiltered samples. Oxidized iron and precipitated sulfide concentrations (particulate and suspended) were estimated by difference between unfiltered and filtered samples. Samples for determination of sulfate and nitrate were unfiltered. Alkalinities were determined titrimetrically using commercially available reagents (Hach, Co.). Total organic carbon (TOC) samples were collected into pre-cleaned amber glass bottles and chilled (4 °C) until analysis using EPA Method 415.2. Samples for volatile organics analyses (BTEX and chlorinated aliphatics) were collected in pre-cleaned, acidified septum vials, and chilled (4 °C) until analyzed by gas chromatography with mass spectrometry using EPA Method 524.2.

2.2.4. Dissolved Gases

H_2 samples were collected using the bubble-strip method (Chapelle and McMahon, 1991) and analyzed at ambient temperatures by gas chromatography (GC) and an RGD2 reduced gas detector (Trace Analytical) within 15 minutes of collection. Standards were prepared with a 100-ppm H_2 in N_2 standard (Scott Specialty Gases). The standard was diluted in stoppered, crimp-sealed serum bottles containing H_2-free N_2 at ambient temperature and pressure. Calibration curves were prepared several times daily and results regressed using a linear model ($P \leq 0.05$). Equilibration of H_2 in ground-water samples was assumed when two samples collected at 5-minute intervals deviated < 5%. Hydrogen was not measured at all wells due to logistical constraints; instead, wells with historically highest contaminant concentrations were sampled. Samples for dissolved methane, ethane and ethene were collected into 1-L septum jars, preserved with concentrated HCl, and chilled (4 °C) until analysis by GC with flame ionization detection (ASTM Method D1945). Dissolved oxygen (DO) was measured with a probe and results confirmed by colorimetric analysis using commercially available reagents (Hach Co.).

2.2.5. Microbiology—Most Probable Numbers (MPNs) and Direct Counts

Ground water samples were collected aseptically into sterile polyethylene bottles and chilled (4 °C) until analysis within 24 h of collection (see section 2.6). Culturable heterotrophic microorganisms in ground water were estimated using miniaturized, 6-tube MPN assays (Braddock and McCarthy, 1996) and 1/5 strength R2A medium (Atlas,

1993). Triplicate assays were incubated at 10 and 25 °C for 3 weeks before scoring. Turbidity was a positive indicator of growth. Results are reported as MPN/mL.

Samples for direct counts were preserved with formalin (3.7% final concentration) until analysis (Braddock et al., 1995). After staining with a 1% solution of acridine orange and filtering known volumes of ground water through a 0.2 μm polycarbonate filter as previously described (Braddock et al., 1984), cells were enumerated using fluorescence microscopy (Olympus). Results are reported as cells/mL.

2.2.6. Microbiology—Anaerobic Heterotrophic Activity (Glutamate Mineralization Potentials)

To examine the effect of temperature on anaerobic heterotrophic activity, mineralization potentials of a readily oxidizable carbon source (U-^{14}C-L-glutamate diluted in 2.5% $NaCl_{(aq)}$) were measured. Ground-water samples were collected by overfilling sterile, polyethylene bottles for several minutes avoiding sample agitation and aeration. Samples were quickly capped, carefully avoiding the formation of a headspace so as minimize exposure to atmospheric oxygen and chilled (4 °C) until analysis within 24 hours of collection. Ten-mL aliquots of samples were aseptically transferred under nitrogen to sterile, oxygen-free 40 mL septum vials and vials were spiked with 100 μg of radiolabeled glutamate (54,100 decays per minute). To simulate in situ conditions, no additional electron donors or nutrients were added. Triplicate vials were incubated in the dark at 10 and 25 °C for 72 hours. Microbial activity was stopped with the addition of 10N NaOH. Afterwards, concentrated HCl was added to liberate CO_2, which was then

trapped in 7.5 mL scintillation cocktail (ICN Radiochemicals) basified with 2.5 mL β-phenyl-ethylamine (Sigma). Radioactivity of trapped $^{14}CO_2$ was measured with a Beckman LS6000SE scintillation counter and glutamate mineralization potentials were calculated using previously described methods (Brown et al., 1991).

2.2.7. Thermodynamic Calculations for Terminal Electron Accepting Processes (TEAPs)

In situ Gibbs free energies for hydrogen-oxidizing TEAPs (ΔG_r) were calculated using the equations and thermochemical data presented in Table 1. Specific activities of relevant chemical species were estimated using geochemical data collected as described above and WEB-PHREEQ (Saini-Eidukat and Yahin, 1999), a web-based interface to PHREEQC (Parkhurst, 1995).

Individual corrections for in situ temperatures were made using the Van't Hoff equation in the form:

$$\Delta G^{T2} = \frac{\Delta H°(298.15\ °K - T_2) + (T_2 \Delta G°)}{298.15\ °K} \qquad (1)$$

where $\Delta G°$ is the Gibbs free energy of reaction for the given TEAP at standard temperature and pressure (STP), ΔG^{T2} is the Gibbs free energy for that TEAP at in situ ground-water temperature, $\Delta H°$ is the enthalpy of reaction at STP, and T_2 is the in situ ground-water temperature in degrees Kelvin (Stumm and Morgan, 1981). When determining whether iron or sulfate reduction was thermodynamically favorable, ΔG_r

values below the reported threshold of about –7 to –15 kJ/mol were used (Hoehler et al., 1994; Westermann, 1994; Jakobsen et al., 1998); for methanogenesis, a threshold value of about –20 kJ/mol CH_4 was used (Conrad, 1999).

2.2.8. Statistical Analyses

Statistical analyses (ANOVA, linear regression, and non-linear regression using a first order decay model) were performed using Systat 7.0 (SPSS, Inc.). Results were considered statistically significant if $P \leq 0.05$. The Mann-Kendall nonparametric test for trends was used to determine if changes in ground water contaminant concentration over time were significant (Gilbert, 1987).

2.3. Results

2.3.1. Inorganic Analyses

Ground water at this site is naturally anaerobic, with DO ranging between < 0.05 and 0.8 mg/L. In September 2000, ground water temperatures were between 1.6 and 8.8 °C (3.7 ± 0.4 °C; mean ± standard error). pH is near neutral (7.1 ± 0.1; mean ± standard error). Nitrate concentrations were below detection limits (< 0.5 mg/L as NO_3-N) in all samples. Oxidation-reduction potentials were generally low (-120 to +90 mV) with no obvious trend in distribution. Ferrous iron concentrations ranged between 0.1 and 4.2 mg/L (Fig. 2a) and ferric iron, presumably present as particulate and/or colloidal $Fe(OH)_3$ was generally ≤ 0.01 (mg/L); one well had 1.2 mg/L (Fig. 2b). Sulfate concentrations

were substantial (21 ± 1 mg/L; mean ± standard error, Fig. 2c) and dissolved sulfide concentrations ranged between < 0.002 and 0.035 mg/L, with the highest concentration at MW20 (Fig. 1). At most wells, concentrations of suspended sulfide were within method detection limits (0.002 µg/L; data not shown). Alkalinities ranged between 86 and 192 mg/L (as $CaCO_3$) and did not vary significantly with distance or depth (Fig. 2d). Methane concentrations were generally low (< 20 - 890 µg/L; Fig. 2e) as was total organic carbon (2.5 ± 0.3 mg/L; mean ± standard error, Fig. 2f) and did not vary significantly with distance or depth.

Dissolved hydrogen concentrations ranged between 0.11 and 2.05 nM. At only one well, MW20 (Fig. 1), was the hydrogen concentration within the range typically characteristic of sulfate-reduction (2.05 nM; Lovely et al., 1994). Hydrogen concentrations at two wells were between iron- and sulfate-reducing ranges (MW5 and MW16). While most hydrogen concentrations suggested that iron-reduction was the predominant TEAP (0.1 - 0.8 nM; Lovely et al., 1994), other geochemical data suggested that sulfate reduction might also have occurred at those same wells. Although present in small quantities, sulfide is indicative of active sulfate reduction; calculated in situ Gibbs free energies support this interpretation (Table 2). At all wells, iron and sulfate reduction were energetically favorable in spite of low hydrogen concentrations ($-\Delta G_r \geq 7$ to 15 kJ/mol). Methanogenesis via H_2/CO_2 was feasible at only one well, MW20, which also had the highest H_2 concentration.

2.3.2. Organic Analyses

TCA concentrations generally decreased with time and were below the maximum contaminant limit (MCL; 200 µg/L) in all samples. Concentrations in September 2000 were between < 0.05 and 31 µg/L, with the highest concentration at MW23 (Fig 1.). Trends in TCE concentrations (i.e., increasing, stable, or decreasing) were not consistent throughout the contaminant plume(s) (Fig. 3). At some wells, concentrations decreased significantly with time while at others, TCE increased or showed no trend. Concentrations of chlorinated aliphatics at up-gradient monitoring wells MW5, MW17, and MW18 have decreased significantly with time since first measured in 1994 (Figs. 3 and 4a-c). Maximum potential rate constants for removal of TCE at these wells were calculated from measured contaminant concentrations. Assuming pseudo first-order decay, rate constants were 0.11, 0.14, and 0.15 $years^{-1}$, respectively, with corresponding half-lives of 6.6, 4.9, and 4.7 years. Low concentrations of partially dechlorinated intermediates of TCE and TCA degradation (i.e., *cis*-1,2-dichloroethene [*cis*-DCE], *trans*-DCE, 1,1-DCE, and dichloroethanes [DCA]) were detected at these wells, and provide evidence of partial reductive dechlorination; vinyl chloride, ethene, and ethane were not detected (not all data shown). Although DCEs and DCAs have consistently been detected at these three wells, relative proportions of these intermediates to parent compounds have not changed over time (i.e., intermediate concentrations have not increased), thereby suggesting that reductive dechlorination has since stopped and that dilution is the primary natural attenuation mechanism. BTEX concentrations at these up-

gradient wells were below MCL (5 μg/L) as early as1994 (MW5) or 1996 (MW17 and MW18).

Most down-gradient wells showed no statistically significant trends in TCE concentrations. At those wells, concentrations remained stable with only minor fluctuations since monitoring began (Fig. 3). At one sampling point, MW13, TCE concentrations have risen although the increase was slight. As with up-gradient wells, partially dechlorinated intermediates of TCE and TCA have consistently been detected at most wells and relative proportions of intermediates to parent compounds have not changed in the down-gradient portions of the plume (Shannon & Wilson, 2000). TCE concentrations have consistently been higher at middle depths (7 –10 m bgs) of the contaminant plume and remained so during the 2000 sampling season (Fig. 5). A substantial number of wells sampled currently exceed the MCL for TCE and do not show a decreasing trend (Fig. 3). By September 2000, toluene, ethylbenzene, and xylenes were all below their respective MCL at all wells tested. Benzene concentrations ranged between < 0.02 and 210 μg/L over the course of this study and have decreased substantially at all sampling points. Currently, benzene above the MCL was detected at only one well, MW103 (7.6 μg/L).

2.3.3. Microbiology

MPNs of culturable aerobic heterotrophs were low, generally less than 1.0×10^4 MPN/mL; estimates were significantly higher at 2 wells, MW13 and MW14, where numbers were $>10^5$ MPN/mL (Fig. 6a). In 50% of samples, MPNs were significantly

lower when assays were incubated at 10 than at 25 °C. Similarly, in all samples tested, anaerobic glutamate mineralization potentials were significantly lower at 10 than at 25 °C (Fig. 6b); little or no activity was observed at 10 °C. Mineralization potentials at either incubation temperature were not higher in samples with higher MPNs. Although MPNs of culturable aerobic heterotrophs and anaerobic mineralization potentials were low when incubated at 10 °C, direct counts of microorganisms were $>10^7$ cells/mL in most samples (Fig. 6c). Microscopic examination of cells revealed numerous spores and very few actively dividing cells in all samples (data not shown).

2.4. Discussion

We examined biogeochemistry and microbiology associated with natural attenuation of BTEX and chlorinated aliphatics in permanently cold, subarctic ground water. At the beginning of this study, concentrations of benzene and TCE, although low, were well above the MCL and implementation of some treatment strategy was necessary to bring this drinking water source into regulatory compliance. The extraordinarily large volume of water requiring treatment (an estimated 1 million cubic meters) coupled with very low contaminant concentrations rendered any engineered solution prohibitively expensive and therefore, a natural attenuation feasibility study was undertaken.

2.4.1. Microbiological Analyses

Laboratory assays can yield useful information when assessing the feasibility of bioattenuation. In this case, glutamate mineralization potentials, an overall indicator of heterotrophic activity, suggested that microorganisms at this site did not function optimally at in situ temperatures. MPNs were greater in 50% of samples and mineralization potentials were significantly greater in 100% of samples when incubated at 25 °C than in those incubated at 10 °C (Fig.6). Several samples were also incubated at 4 °C, which is closer to actual in situ temperatures, and activity in those assays was even lower than that observed at 10 °C (data not shown). Similar results were observed at another local site with considerable BTEX contamination; substantial mineralization of glutamate and benzene did not occur at temperatures below 15 °C (Braddock et al., 1998). The fact that heterotrophic activity was greater at 25 °C implies that the microbial community present is psychrotolerant (i.e., capable of growth at colder temperatures but functioning optimally at temperatures between 25 and 30 °C). This is notable in that ground water at this and other subarctic sites is permanently cold, varying by only a few degrees during the year (Krumhardt, 1982; Flynn, 1985; Downey and Sinton, 1990; Braddock et al., 1998; Hinzman et al., 2000; this study). While microorganisms present in ocean floor sediments have adapted to growth at permanently cold temperatures (Brock and Madigan, 1991), this apparently is not the case at Six Mile Village. Further support for this interpretation is provided by microscopic examination. Although there are numerous cells present, many cells had sporulated and few were actively dividing (data not shown). These data and observations suggest that even with an ample supply of readily oxidizable substrate (such as BTEX), electron acceptor and nutrients,

biodegradation rates are likely to be much lower at this site than those seen in more temperate climates.

2.4.2. Biogeochemistry and Thermodynamics of TEAPs

Establishing whether natural attenuation offers a suitable means of treatment is not necessarily a straightforward exercise, particularly in cold, dilute ground water systems. An accurate determination of a predominant TEAP is essential and at this site, that determination was difficult. Although hydrogen concentrations were almost uniformly within the range predicted for iron reduction, this interpretation is dubious because a source of ferric iron is unknown. Aquifer sediments are composed of mafic (containing reduced iron and manganese) minerals (Downey and Sinton, 1990), which, through dissolution, can result in substantial concentrations of ferrous iron. Concentrations of particulate ferric iron were very low, generally < 0.1 mg/L and the presence of oxidized iron in any other form (i.e., as a crust on individual grains) has not been confirmed. Conversely, sulfate concentrations are relatively high—about 20 mg/L—and because aqueous ferrous iron and sulfide precipitate readily, the presence of aqueous sulfide is indicative of local production (Christensen et al., 1994). In addition to these considerations, no significant spatial or temporal trends in distribution of electron acceptors and reduced end products were observed and, therefore, provided no evidence of prevailing TEAPs. Anaerobic mineralization assays and microscopic examination of ground-water microorganisms suggested that microbial activity at this site is low due to sub-optimal growth conditions. It is conceivable that iron and sulfate reduction co-occur

at low rates (assuming ferric iron is available), but neither process dominates because the prevailing conditions in this very cold system render indigenous microbial populations poorly competitive. This prohibits any one terminal metabolic group from sequestering the majority of electron flow and the subsequent formation of distinctly different TEAP zones.

The report of concurrent TEAPs is not novel (Christensen, et al., 2000 and references therein). Concurrent iron and sulfate reduction has been reported at the Norman Landfill, Oklahoma (Cozzarelli et al., 2000), the Grindsted Landfill, Denmark (Jakobsen et al., 1998), and a shallow pristine aquifer in Rømø, Denmark (Jakobsen and Postma, 1999). Concurrent sulfate reduction and methanogenesis has also been reported (Jakobsen et al., 1998; Vroblesky et al., 1996) as well as concurrent nitrate and iron reduction (Broholm et al., 2000). Biogeochemical evidence suggests that TEAPs may have co-occurred at Six Mile Village and although this determination is not conclusive, ΔG_r values calculated using in situ concentrations of reactants and products indicate that both iron and sulfate reduction were energetically feasible at all wells.

Favorable free energies for multiple TEAPs appear to be partially the result of low temperature and high electron donor concentrations (Hoehler et al., 1998). By inserting 15 °C into the Nernst equation (Table 1) instead of the measured in situ temperature (ca. 4 °C), ΔG_r values for individual TEAPs increase by about 10 kJ/mol. Several other studies have demonstrated that low temperatures enable terminal metabolic processes to proceed at lower partial pressures of hydrogen than those typically seen at

higher temperatures (Westermann, 1994; Hoehler et. al., 1998; Jakobsen et al., 1998; Jakobsen and Postma, 1999).

Similarly, high concentrations of sulfate may permit substantial sulfate reduction in spite of low concentrations of hydrogen (Westermann, 1994; Hoehler et al., 1998). By reducing sulfate concentrations used in calculations by approximately an order of magnitude to 2 mg/L, calculated ΔG_r values for sulfate reduction at Six Mile Village become less favorable by approximately 5 kJ/mol for all sampling points. It is interesting to note that, while the ΔG_r values for iron and sulfate reduction were thermodynamically feasible, they were considerably more exergonic (i.e., more negative) than previously reported threshold values of ca. –7 to –15 kJ/mol at other sites (Westermann, 1994; Hoehler et al., 1994; Jakobsen et al., 1998). This implies that ground water in this system is farther from equilibrium than ground water at other sites, perhaps due to very low microbial activity (see section *4.1*).

While it seems plausible that iron and sulfate reduction co-occurred, several lines of evidence support the conclusion that methanogenesis was not an important reaction at this site. Methane concentrations were low in most wells tested (Table 2) and while its presence is generally indicative of active methanogenesis, this assumption may be incorrect in this case. Methane in local ground water has been associated with permafrost and peat, present throughout the region (Péwé et al., 1976; Kvenvolden and Lorenson, 1993); its presence at this site may simply reflect diffusion from methanogenic sources and this interpretation is supported by thermodynamic calculations (Table 2). Numerous studies have calculated ΔG_r for H_2-dependent methanogenesis and most values reported

were between –20 and –50 kJ/mol (Conrad, 1999 and references cited therein). By this criterion, H_2-dependent methanogenesis was energetically feasible at only one well sampled. Because sulfate concentrations are not limiting and hydrogen concentrations are very low, it is likely that H_2-dependent methanogenesis at this site could only occur in stagnant porewater with lower sulfate and increased hydrogen concentrations or via interspecies hydrogen transfer.

It is not entirely certain whether iron or sulfate reduction dominated at this site but the presence of partially dechlorinated intermediates suggests that redox conditions were favorable for reductive dechlorination of TCE and TCA, at least at some time in the past or in some portions of the plume. However, because these intermediates were present in early samplings and relative proportions of intermediates and parent compounds did not change, it seems most likely that reductive dechlorination occurred in the past and has since stopped. Possible explanations for this conclusion include low concentrations and/or poor quality of electron donors or transport of contaminants to a more oxidized environment. Although reductive dechlorination via chlororespiration has been observed in the laboratory at threshold hydrogen concentrations typically suggestive of iron reduction (< 0.3 nM; Löffler et al., 1999), this phenomenon has not yet been demonstrated in situ. In addition, even if one assumes conditions were sufficient to support reductive dechlorination via the metabolic activity of sulfate-reducing bacteria, extremely low concentrations of chlorinated aliphatics relative to sulfate place a severe kinetic constraint on the utility of this process for bioattenuation at this site. It may be that reductive dechlorination occurred shortly after the initial spill, when concentrations

of TCE, TCA, and BTEX were highest, then ceased as contaminant concentrations declined as a result of advective transport and diffusion, or biodegradation in the case of BTEX.

It is probable that biodegradation of some BTEX components occurred. Soil/water partition coefficients (K_d) for benzene and toluene are similar (0.37 and 0.84 mL/g; U.S. EPA, 2000) and therefore, the two compounds are expected to travel through ground water at similar velocities. However, toluene has been undetected for several years while benzene persists, indicating that biological degradation of toluene likely occurred at this site. This is consistent with the results of a review study that determined median rate constants for benzene biodegradation were approximately an order of magnitude lower than those observed for toluene at 133 different sites (0.3% and 4% day^{-1}, respectively; Suarez and Rifai, 1999). Ethylbenzene and xylenes have also been undetected for some time suggesting that these contaminants were biologically degraded or were adsorbed to aquifer minerals.

In addition to the difficulties encountered when ascertaining TEAPs at this site, generally reliable natural attenuation signals may have been obscured by naturally occurring geochemistry. Concentrations of contaminants capable of serving as electron donors (BTEX) were sufficiently low, especially at the end of this study, that any signal of their bioattenuation would be masked by relatively high, normally fluctuating concentrations of sulfate, carbonate, and ferrous iron. Similarly, relatively high concentrations of chloride (2 – 7 mg/L; Shannon & Wilson, 2000) would obscure the expected µg/L increase in chloride resulting from reductive dechlorination of chlorinated

aliphatics at this study site. Further confounding the issue is the fact that ground-water sulfate concentrations normally fluctuate. Even if BTEX compounds were present in higher concentrations and biodegradation did occur via sulfate reduction, a significant decrease in sulfate concentrations might not be evident. This situation has been reported previously (Plummer et al., 1990; Chapelle et al., 1995).

While site managers, scientists and engineers might use sound, scientifically based reasoning to determine that natural attenuation represents the most viable, economical treatment option for a particular contaminated site, they must be aware of potential community concerns when implementing this approach, particularly at sites such as this where it appears that dilution and dispersion may be the dominant contaminant-reduction processes. Due to low contaminant concentrations, high concentrations of sulfate, chloride and alkalinity, uncertain TEAP determinations, and extremely low microbial activity, this study was not able to conclusively document footprints characteristic of bioattenuation. Given similar difficulties at other comparable sites (Hinzman et al., 2000; Richmond and Braddock, 2000), it seems likely that natural attenuation of chlorinated solvents, and perhaps BTEX, might be not an appropriate treatment strategy at this and other subarctic sites with similar geochemistry. In addition, sediment microcosms designed to examine contaminant transformation and measurement of in situ organic acids (Cozzarelli et al., 1990), may be essential analyses when attempting to document bioattenuation of BTEX and chlorinated aliphatics in this and other dilute systems.

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2.6. Literature Cited

Atlas, R.M., 1993. *Handbook of Microbiological Media*. Boca Raton, FL, CRC Press, 1079 pp.

Beller, H.R., Grbić-Galić, D., Reinhard, M., 1992. Microbial degradation of toluene under sulfate-reducing conditions and the influence of iron on the process. Appl. Environ. Microbiol. 58, 3192-3195.

Braddock, J.F., Luong, H.V., Brown, E.J., 1984. Growth kinetics of *Thiobacillus ferrooxidans* isolated from arsenic mine drainage. Appl. Environ. Microbiol. 48, 48-55.

Braddock, J.F., Lindstrom, J.E., Brown, E.J., 1995. Distribution of hydrocarbon-degrading microorganisms in sediments from Prince William Sound, Alaska, following the *Exxon Valdez* oil spill. Mar. Pollut. Bull. 30, 125-132.

Braddock, J.F., McCarthy, K.A., 1996. Hydrologic and microbiological factors affecting persistence and migration of petroleum hydrocarbons spilled in a continuous-permafrost region. Environ. Sci. Technol. 30, 2626-2633.

Braddock, J.F., Catterall, P., Richmond, S.A., 1998. Assessment of the potential for biodegradation of petroleum hydrocarbons in the Railroad Industrial Area, Fairbanks, Alaska, 1993-1994. U.S. Geological Survey Open-File Report 98-287.

Brock, T.D., Madigan, M.T., 1991. *Microbiology of Microorganisms*, 6th ed. Prentice Hall, Englewood Cliffs, NJ. 876 pp.

Broholm, M.M., Crouzet, C., Arvin, E., Cristophe, M., 2000. Concurrent nitrate and Fe(III) reduction during anaerobic biodegradation in a sandstone aquifer. J. Contam. Hydrol. 44, 275-300.

Brown, E.J., Resnick, S.M., Rebstock, C., Luong, H.V., Lindstrom, J.E., 1991. UAF radiorespirometric protocol for assessing hydrocarbon mineralization potential in environmental samples. Biodegradation 2, 121-127.

Chapelle, F.H., McMahon, P.B., 1991. Geochemistry of dissolved inorganic carbon in a Coastal Plain aquifer. 1. Sulfate from confining beds as an oxidant in microbial CO_2 production. J. Hydrol. 127, 85-108.

Chapelle, F.H., McMahon, P.B., Dubrovsky, N.M., Fujii, R.F., Oaksford, E.T., Vroblesky, D.A., 1995. Deducing the distribution of terminal electron-accepting processes in hydrologically diverse ground water systems. Water. Resour. Res. 31, 359-371.

Christensen, T.H., Kjeldsen, P., Albrechtsen, H.-J., Heron, G., Nielsen, P.H., Bjerg, P.L., Holm, P.E., 1994. Attenuation of landfill leachate pollutants in aquifers. Crit. Rev. Environ. Sci. Technol. 24, 119-202.

Christensen, T.H., Bjerg, P.L., Banwert, S.A., Jakobsen, R., Heron, G., and Albrechtsen, H.-J., 2000. Characterization of redox conditions in ground water contaminant plumes. J. Contam. Hydrol. 45, 165-241.

Conrad, R., 1999. Contribution of hydrogen to methane production and control of hydrogen concentrations in methanogenic soils and sediments. FEMS Microbiol. Ecol. 28, 193-202.

Cozzarelli, I.M., Eganhouse, R.P., and Baedecker, M.J., 1990. Transformation of monoaromatic hydrocarbons to organic acids in anoxic ground water environment. Environ. Geol. Water Sci. 16, 135-141.

Cozzarelli, I.M., Suflita, J.M., Ulrich, G.A., Harris, S.H., Scholl, M.A., Schlottmann, J.L., Christenson, S., 2000. Geochemical and microbiological methods for evaluating anaerobic processes in an aquifer contaminated by landfill leachate. Environ. Sci. Technol. 34, 4025-4033.

Downey, J.S., Sinton, P.O., 1990. Geohydrology and ground-water geochemistry at a sub-arctic landfill, Fairbanks, Alaska. U.S. Geological Survey Water-Resources Investigations Report 90-4022.

Evans, P.J., Mang, D.T., Kim, K.S., Young, L.Y., 1991a. Anaerobic degradation of toluene by a denitrifying bacterium. Appl. Environ. Microbiol. 57, 1139-1145.

Evans, P.J., Mang, D.T., Kim, K.S., Young, L.Y., 1991b. Degradation of toluene and *m*-xylene and transformation of *o*-xylene by denitrifying enrichment cultures. Appl. Environ. Microbiol. 57, 450-454.

Flynn, D.M., 1985. Hydrology and geochemical processes of a subarctic landfill, Fairbanks, Alaska: Basic data. U.S. Geological Survey Open-File Report 85-195.

Gilbert, R.O., 1987. *Statistical Methods for Environmental Pollution Monitoring*, John Wiley & Sons, Inc., New York, 320 pp.

Glass, R.L., Lilly, M.R., Meyer, D.F., 1996. Ground-water levels in an alluvial plain between the Tanana and Chena Rivers near Fairbanks, Alaska, 1986-93. U.S. Geological Survey Water-Resources Investigations Report 96-4060.

Hinzman, L.D., Lilly, M.R., Braddock, J.F., McCarthy, K.A., Richmond, S.A., Wegner, M.A., 2000. Natural attenuation of chlorinated-hydrocarbon contamination at Fort Wainwright, Alaska; A hydrogeochemical and microbiological investigation. Institute for Northern Engineering/Water and Environmental Research Center. University of Alaska Fairbanks. Report 00.02.

Hoehler, T.M., Alperin, M.J., Alberts, D.B., Martens, C.S., 1994. Field and laboratory studies of methane oxidation in anoxic marine sediment: Evidence for a methanogen-sulfate reducer consortium. Global Biogeochem. Cycles. 8, 451-463.

Hoehler, T.M., Alperin, M.J., Alberts, D.B., Martens, C.S., 1998. Thermodynamic control on hydrogen concentrations in anoxic sediments. Geochim. Cosmochim. Acta 62, 1745-1756.

Jakobsen, R., Albrechtsen, H.J., Rasmussen, M., Bay, H., Bjerg, P.L., Christensen, T.H., 1998. H_2 concentrations in a landfill leachate plume (Grindsted, Denmark): In situ energetics of terminal electron acceptor processes. Environ. Sci. Technol. 32, 2142-2148.

Jakobsen, R., Postma, D., 1999. Redox zoning, rates of sulfate reduction and interactions with Fe-reduction and methanogenesis in a shallow sandy aquifer, Rømø, Denmark. Geochim. Cosmochim. Acta 63, 137-151.

Krumhardt, A.P., 1982. Hydrologic information for land-use planning, Badger Road area, Fairbanks, Alaska. U.S. Geological Survey Water Resources Investigations Report 82-4097.

Kvenvolden, K.A, Lorenson, T.D., 1993. Methane in permafrost—preliminary results from coring at Fairbanks, Alaska. Chemosphere 26, 609-616.

Langmuir, D., 1997. *Aqueous Environmental Geochemistry*. Prentice-Hall, Inc., New Jersey, 600 pp.

Löffler, F.E., Tiedje, J.M., Sanford, R.A., 1999. Fraction of electrons consumed in electron acceptor reduction and hydrogen thresholds as indicators of halorespiratory physiology. Appl. Environ. Microbiol. 65, 4049-4056.

Lovely, D.R., Chapelle, F.H., Woodward, J.C., 1994. Use of dissolved H_2 concentrations to determine distribution of microbially catalyzed redox reactions in anoxic ground water. Environ. Sci. Technol. 28,1205-1210.

Lovely, D.R., 1997. Potential for anaerobic bioremediation of BTEX in petroleum-contaminated aquifers. J. Indust. Microbiol. 14, 85-93.

Nakanishi, A.S., Lilly, M.R., 1998. Estimate of aquifer properties by numerically simulating ground-water/surface-water interactions, Fort Wainwright, Alaska. Water-Resources Investigations Report 98-4088.

National Research Council (NRC), 2000. Natural Attenuation for Ground water Remediation/Committee on Intrinsic Remediation, Water Science and Technology Board [and] Board on Radioactive Waste Management, Commission on Geosciences, Environment, and Resources. National Academy Press, Wash., D.C. 274 pp.

Nelson, G.L., 1978. Hydrologic information for land-use planning, Fairbanks vicinity, Alaska. U.S. Geological Survey Open-File Report 78-959.

Parkhurst, D.L., 1995. Users Guide to PHREEQC. U.S. Geological Survey Investigative Report 95-4227.

Péwé, T.L., Bell, J.W., Forbes, R.B., Weber, F.R., 1976. Geologic map of the Fairbanks D-2 SW quadrangle, Alaska. U.S. Geological Survey Miscellaneous Investigations Series Map I-829-A, scale, 1:24,000, 1 sheet.

Plummer, L.N., Busby, J.F., Lee, R.W., Hanshaw, B.B., 1990. Geochemical modeling of the Madison aquifer in parts of Montana, Wyoming, and South Dakota. Water Resour. Res. 26, 1981-2014.

Richmond, S.A., Braddock, J.F., 2000. Geochemical characterization of anaerobic ground water in subarctic Alaska. Proceedings of the American Water Research Association Conference: Water Resources in Extreme Environments. Middleburg, Virginia, TPS-99-4, pp. 141-145.

Saini-Eidukat, B. and Yahin, A., 1999. Web-phreeq: A WWW instructional tool for modeling the distribution of chemical species in water. Computers & Geosciences, 25, 347-353.

Shannon & Wilson, Inc., 1994. Arctic Surplus Salvage Yard, remedial investigation/feasibility study, Fairbanks, Alaska, remedial investigation report. Report prepared for the Alaska District, U.S. Army Corps of Engineers.

Shannon & Wilson, Inc., 1998. Final conceptual site model, tracts 1 and 2, Groff subdivision, Denny properties, Fairbanks, Alaska. Report prepared for the Alaska Department of Environmental Conservation, Contract 18801753.

Shannon & Wilson, Inc., 2000. Ground water monitoring and evaluation of natural attenuation, Six Mile Richardson Highway, Fairbanks, Alaska. Prepared for the Alaska Department of Environmental Conservation.

Stumm, W., Morgan, J.J., 1981. *Aquatic Chemistry* (2^{nd} ed.), John Wiley and Sons, Inc. NY, NY. 780 pp.

Suarez, M.P., Rifai, H.S., 1999. Biodegradation rates for fuel hydrocarbons and chlorinated solvents in ground water. J. Biorem. 3, 337-362.

U.S. Environmental Protection Agency (US EPA), 1997. *Cleaning Up the Nation's Waste Sites: Markets and Technology Trends.* 1996 edition. EPA 542-R-96-005. Washington, D.C.: EPA, Office of Solid Waste and Emergency Response.

U.S. Environmental Protection Agency (US EPA), 2000. Physical-Chemical Data for Volatile Organic Compounds. http://www.epa.gov/region09/waste/sfund/prg/s5_01.htm and http://www.epa.gov/region09/waste/sfund/prg/s5_02.htm. Accessed February 2001.

Vogel, T.M., Grbić-Galić, D., 1986. Incorporation of oxygen from water into toluene and benzene during anaerobic fermentative transformation. Appl. Environ. Microbiol. 5, 200-202.

Vogel, T.M., Criddle, C.S., McCarty, P.L., 1987. Transformations of halogenated aliphatic compounds. Environ. Sci. Technol. 21, 722-736.

Vroblesky, D.A., Bradley, P.M., Chapelle, F.H., 1996. Influence of electron donor on the minimum sulfate concentration required for sulfate reduction in a petroleum hydrocarbon-contaminated aquifer. Environ. Sci. Technol. 30, 1377-1381.

Westermann, P., 1994. The effect of incubation temperature on steady-state concentrations of hydrogen and volatile fatty acids during anaerobic degradation in slurries from wetland sediments. FEMS Microbiol. Ecol. 13, 295-302.

Table 2.1. Equations and thermodynamic values used for calculating in situ Gibbs free energies (ΔG_r) for H_2-oxidizing terminal-electron accepting processes (TEAPs)[a]

TEAP	Equation used for calculating in situ ΔG_r	ΔG_r^* (kJ·mol^{-1})	ΔH_r^* (kJ·mol^{-1})
$\frac{1}{2}H_{2(aq)} + Fe(OH)_3 + 2H^+ \rightleftharpoons Fe^{2+} + 3H_2O$	$\Delta G_r = \Delta G^{T\square} + RT \ln \frac{[Fe^{2+}]}{[H_2]^{1/2}[H^+]^2}$	-100.2[b] -87.2[c]	-121.1[d]
$4H_{2(aq)} + SO_4^{2-} + H^+ \rightleftharpoons HS^- + 4H_2O$	$\Delta G_r = \Delta G^{T\square} + RT \ln \frac{[HS^-]}{[H_2]^4[SO_4^{2-}][H^+]}$	-264.1	-235.0
$4H_{2(aq)} + HCO_3^- + H^+ \rightleftharpoons CH_{4(aq)} + 3H_2O$	$\Delta G_r = \Delta G^{T\square} + RT \ln \frac{[CH_4]}{[H_2]^4[HCO_3^-][H^+]}$	-229.3	-237.8

[a] R is the gas constant, T is the absolute temperature in K, [ ] indicate species activity or molarity. Thermodynamic data for solutes from Langmuir (1997) and Stumm and Morgan (1981). [b] slightly aged $Fe(OH)_3$; [c] freshly precipitated $Fe(OH)_3$; [d] ΔH_r^* for goethite used for calculations as ΔH_r^* for $Fe(OH)_3$ has not been determined and temperature effects are slight. Table adapted from Jakobson et al., 1998.

Table 2.2. Calculated in situ Gibbs free energies (ΔG_r) for H_2-oxidizing terminal electron-accepting processes (TEAPs). Bold numbers indicate that the reaction is thermodynamically feasible and may have occurred in situ. All results in kJ/mol.

Well	$Fe(OH)_3$[a] Reduction	$Fe(OH)_3$[b] Reduction	Sulfate Reduction	Methanogenesis
MW5	**-40**	**-25**	**-50**	-17
MW13	**-39**	**-27**	**-44**	-12
MW14	**-33**	**-21**	**-29**	5
MW16	**-37**	**-25**	**-50**	-17
MW17	**-34**	**-22**	**-51**	-12
MW18	**-30**	**-18**	**-32**	-2
MW20	**-31**	**-19**	**-50**	**-20**
MW106	**-38**	**-26**	**-44**	-9
MW107	**-40**	**-28**	**-40**	-6
MW108	**-38**	**-26**	**-42**	-8

[a]slightly aged and [b]freshly precipitated $Fe(OH)_3$.

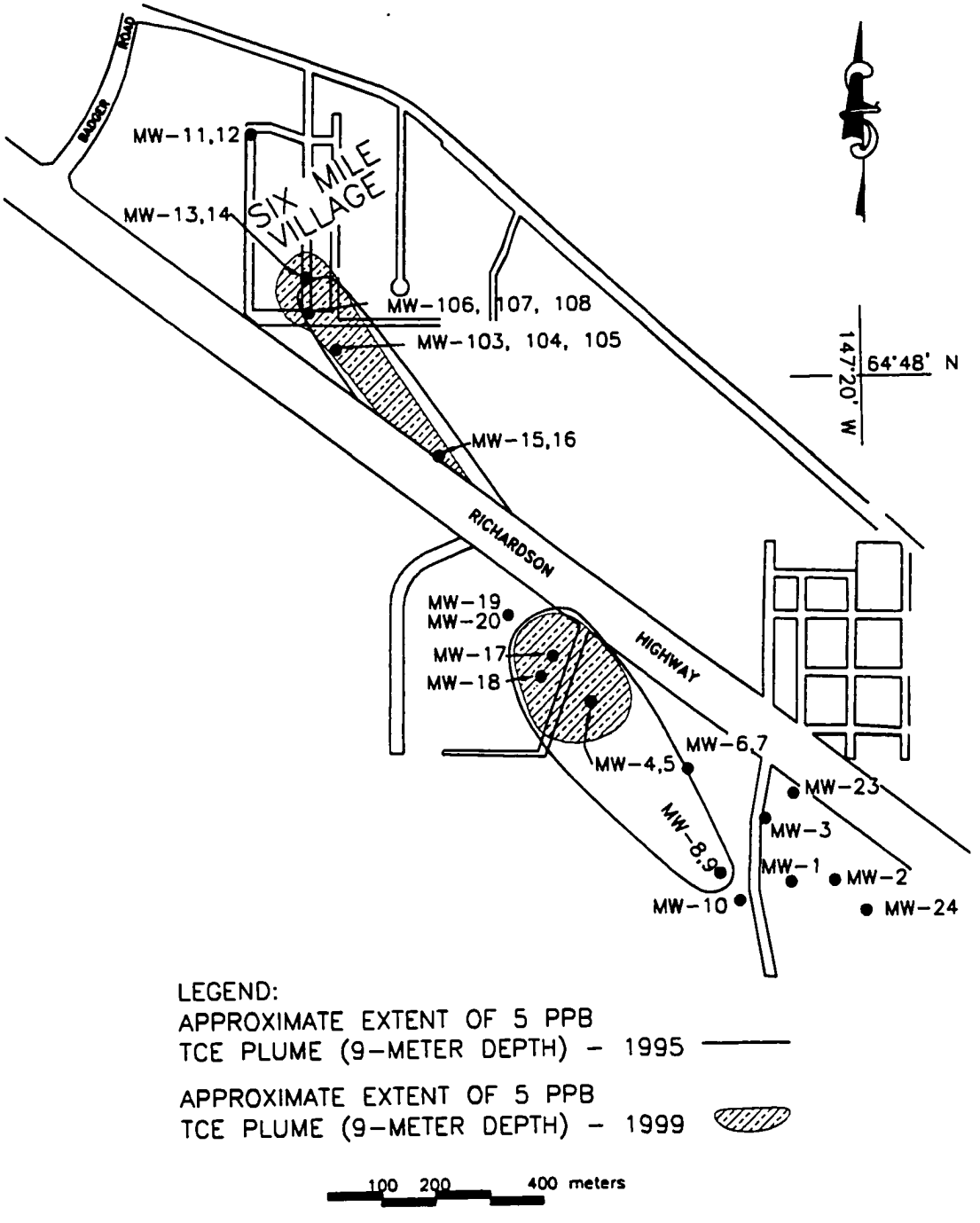

Figure 2.1. Location and map of study area, Six Mile Village, Alaska, showing 5 ppb trichloroethene (TCE) plume boundaries in 1995 (—) and 2000 (▒). • indicates monitoring well.

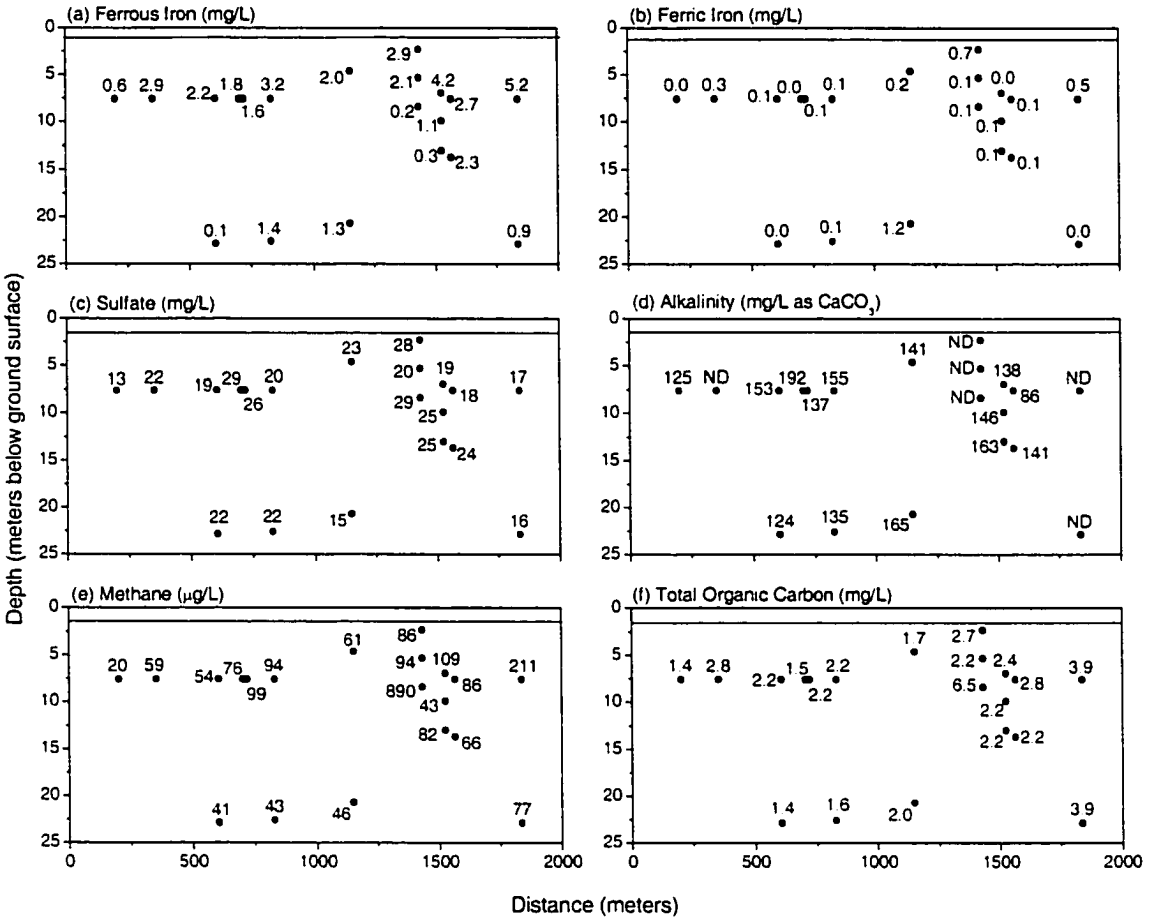

Figure 2.2. Concentrations of ferrous (a) and ferric iron (b), sulfate (c), alkalinity (d), methane (e), and total organic carbon (f) at Six Mile Village, Alaska, September 2000. Concentrations are in mg/L except where noted. • indicates sampling point. Horizontal line near the top of each graph represents approximate location of the water table.

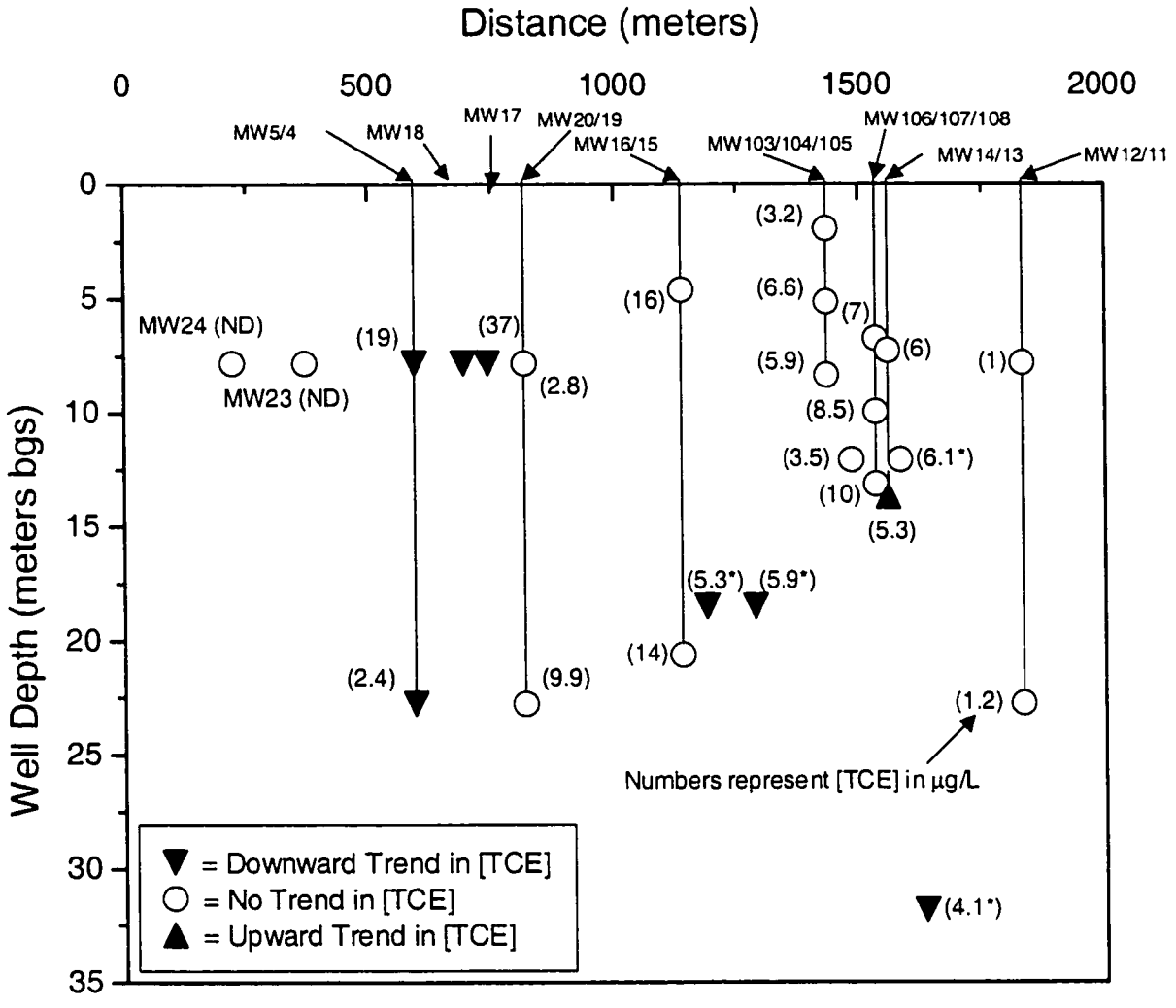

Figure 2.3. Temporal trends in tricholorethene (TCE) concentrations at Six Mile Village, Alaska. Trends in TCE concentrations at individual sampling points are indicated by a ▼(significantly decreasing trend), a ○ (no significant trend), or a ▲(significantly increasing trend). Numbers in parentheses indicate TCE concentrations measured at most recent sampling, September 2000. ND indicates TCE not detected at method detection limit of 0.05 µg/L. * indicates residential well. (Not all residential wells sampled.)

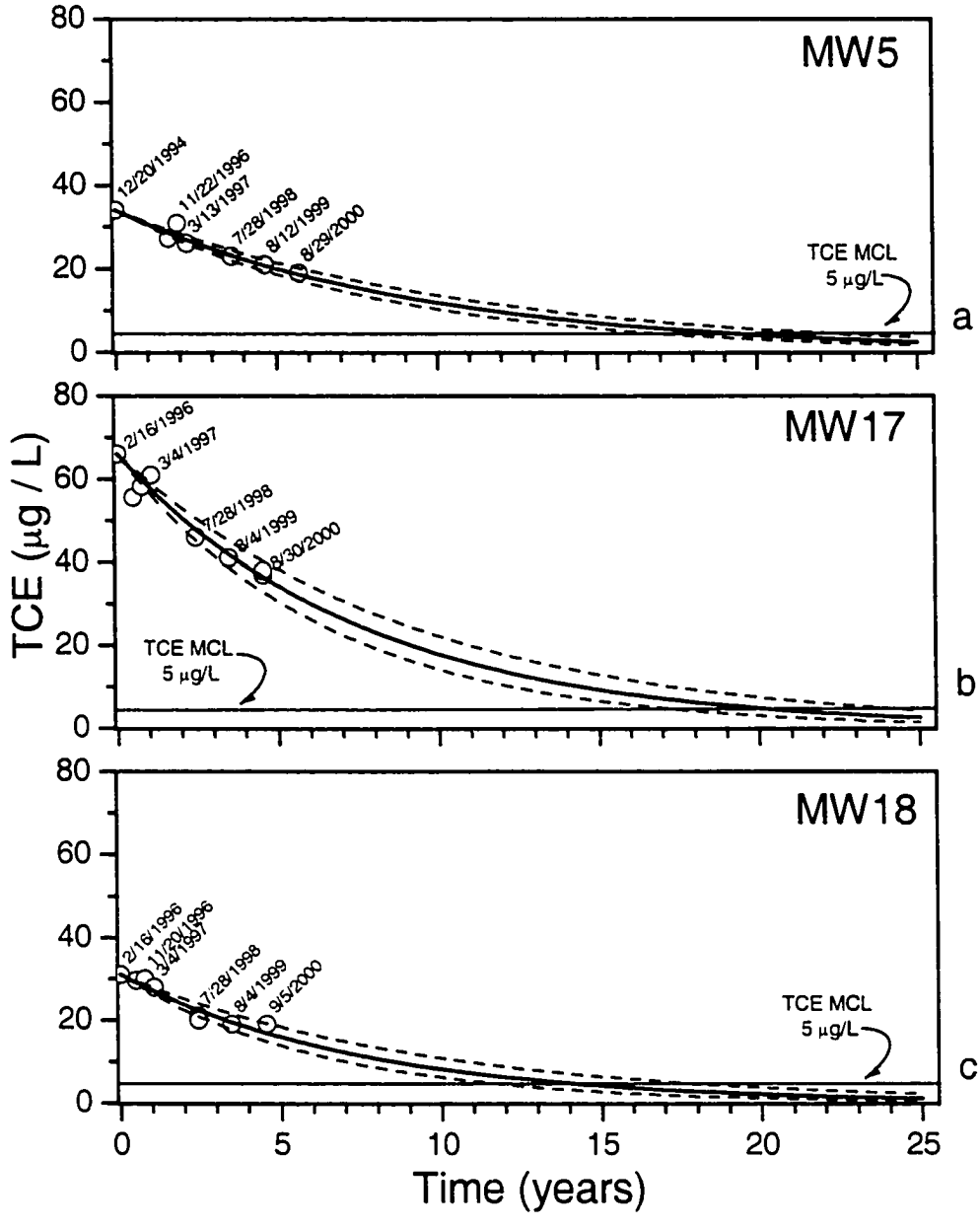

Figure 2.4. Exponential decay of trichloroethene (TCE) at monitoring wells MW5, MW17, and MW18, located in the upgradient portion of TCE contamination at Six Mile Village, Alaska. Solid lines (—) represent non-linear regression estimates assuming pseudo-first order decay; dashed lines (--) represent 95% confidence limits.

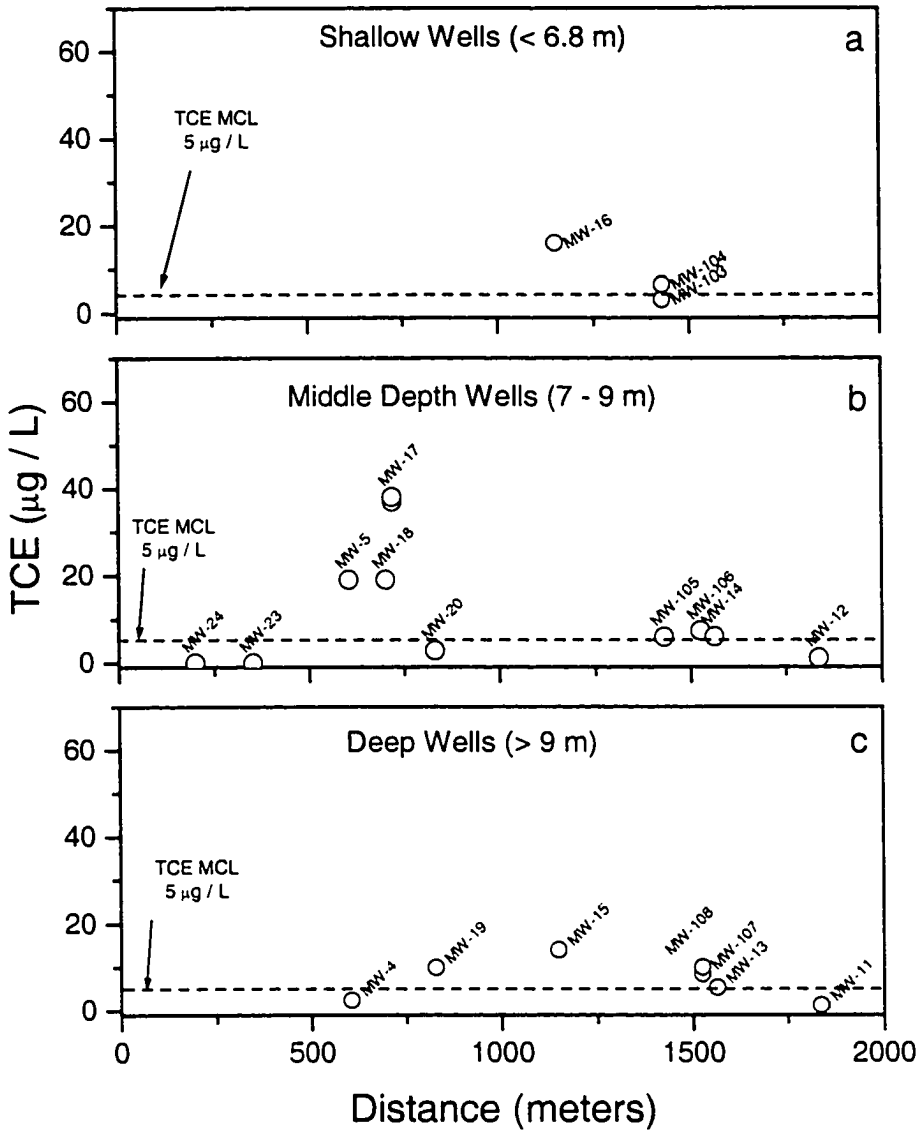

Figure 2.5. Trichloroethene (TCE) concentrations in shallow (≤ 6.6 m bgs; a), mid-depth (6.8 – 9.1 m bgs; b), and deep wells (> 9.1 m bgs; c), Six Mile Village, Alaska, September 2000.

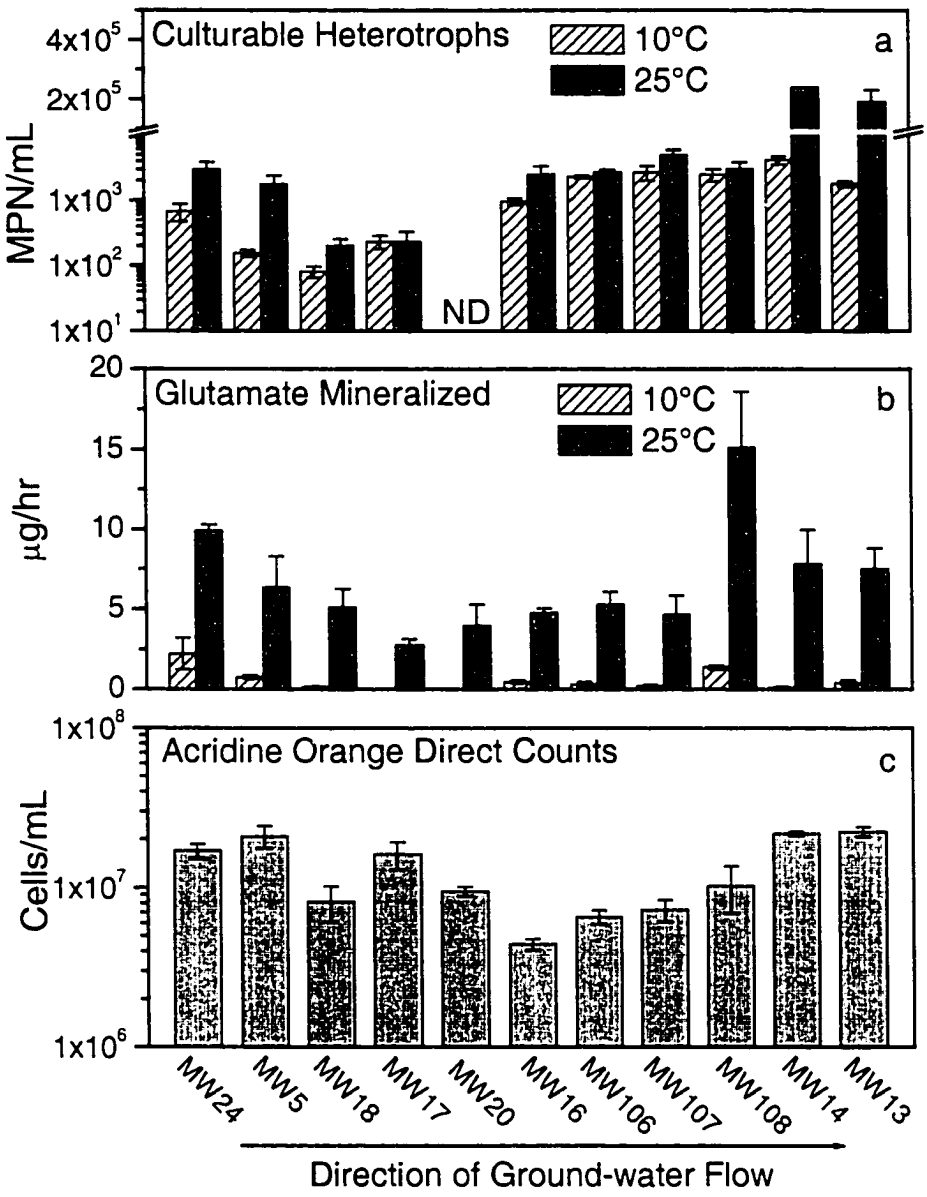

Figure 2.6. Temperature effects on most probable numbers (MPN) of heterotrophic microorganisms (a) and anaerobic heterotrophic activity as measured by glutamate mineralization potentials (b). Note axis break on Figure 6a. Acridine orange direct counts of microorganisms (c). Error bars represent the standard error of triplicate assays. ND indicates no data.

CHAPTER 3

Ground-Water/Surface-Water Interactions in a Subarctic Aquifer: Implications for Natural Attenuation[3]

Abstract

We examined the effects of ground-water/surface-water interactions on ground-water biogeochemistry at Fort Wainwright, Alaska, where ground water was contaminated with trichloroethene (TCE) and substantial quantities of gasoline and diesel fuel. Contaminant plume boundaries had stabilized near the riverbank before active treatment began in 1996, indicating that natural attenuation processes were occurring. Ground water usually discharges into the Chena River but transient flow reversals occur in spring and summer during brief periods when the river is at high stage. At those times, highly oxygenated surface water enters this naturally anaerobic aquifer, causing significant changes in ground-water geochemistry and elevation ($\leq$ 3 m). Near the riverbank, ground water remained anoxic (< 0.8 mg/L), even during recharge. In monitoring wells ca. 90 m from the riverbank, dissolved oxygen concentrations at the water table, although low, were significantly greater during aquifer recharge ($P = 0.002$) than during aquifer discharge likely resulting from oxygenation as ground water rose through the unsaturated zone. Quantities of suspended ferric iron were also greater when measured during aquifer recharge than during aquifer discharge ($P = 0.002$), suggesting that rises in water-table elevations that accompany surface-water influx caused

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precipitation of iron (and probably manganese) hydroxides at the water table. Pore-water concentrations of hydrogen were uniformly indicative of iron- or manganese-reduction but low concentrations of sulfides and methane were present in most samples. Calculated in situ Gibbs free energies for iron and sulfate reduction were energetically feasible at all sampling points and support the hypothesis that these terminal electron-accepting processes may have co-occurred, although metal reduction likely predominated. Methanogenesis via H_2/CO_2 was never energetically feasible. Surface-water influx may have slowed net rates of contaminant transport towards the Chena River by intermittently "pushing" contaminated ground water away from the river; mixing of surface and ground water likely diluted contaminant concentrations near the river. These processes may have been important for the stabilization of plume boundaries near the river. Ground-water/surface-water interactions appeared to cause seasonal oxidation of ground water near the water table, however, conditions remained favorable for the reductive dechlorination of TCE at this subarctic site and, apparently, biodegradation of petroleum hydrocarbons.

Key words: Ground-water/surface-water interactions; Contaminant fate; Terminal electron-accepting processes (TEAPs); Gibbs free energy; Redox; Hydrogen

3.1. Introduction

Numerous studies have investigated ground-water/surface-water interactions although relatively few have examined what effects these interactions may have on contaminant fate and transport. Recent examples include an assessment of agrochemical concentrations in ground water following the catastrophic 1993 flood on the Mississippi

River (Heimann et al., 1997) and investigations of mass transfer of herbicides between surface and ground water (Squillace and Thurman, 1992; Squillace et al., 1997). Lendvay et al. (1998) studied ground-water/surface water interactions related to chlorinated solvent degradation and several groups are currently examining biogeohemical processes associated with municipal landfill-leachate degradation in a transient flow system (Harris et al., 1999; Cozzarelli et al. 2000). Although research has increased in recent years, knowledge of ground-water/surface-water interactions and how they affect contaminant degradation is limited, particularly in subarctic environments. For the purposes of contaminated-site management, a better understanding of how these interactions affect the fate of ground-water contaminants is critical.

Increased reliance on petroleum as an energy source has resulted widespread petroleum-hydrocarbon contamination, affecting surface- and ground-water quality in the U.S. and other countries. Because chlorinated solvents are excellent degreasers, they are frequently found as co-contaminants at many sites. In the U.S., chlorinated ethenes, including tetrachloroethene (PCE), TCE, dichloroethenes (DCE) and vinyl chloride (VC), are the most common ground-water contaminants and represent a significant threat to human health (National Research Council (NRC), 1994). One reason that chlorinated ethenes are so common is that they are highly resistant to biodegradation. As a result, the likelihood that natural attenuation of these persistent contaminants will succeed within reasonable time frames is generally low (NRC, 2000).

Natural attenuation of ground-water contamination encompasses all physical, chemical and biological processes that, without human intervention, reduce contaminant

concentrations or mobility (U.S. EPA, 1999). Biologically mediated natural attenuation processes are diverse and highly dependent upon ambient redox conditions. These reactions are desirable because they are the only naturally occurring processes that can potentially remove the contaminant from the environment instead of immobilizing it (e.g., sorption), transporting it to another place (e.g., dilution and dispersion) or transferring it to another phase (e.g., volatilization).

Many petroleum-hydrocarbon contaminated sites have been successfully remediated via natural attenuation (NRC, 2000). Microbial mineralization and transformation of the gasoline components benzene, toluene, ethylbenzene, and xylenes (BTEX) occur readily under aerobic and, to a lesser extent, anaerobic conditions. These compounds can be degraded by denitrifying, iron- and sulfate reducing, and fermentative microorganisms (Beller et al., 1992; Evans et al., 1991a, b; Lovely, 1997; Vogel and Grbić-Galić, 1986). Recent studies have shown that alkanes and alkenes can also be degraded anaerobically under a variety of electron-accepting conditions (reviewed by Heider et al., 1998).

Unlike petroleum hydrocarbons, which typically are highly amenable to degradation under aerobic conditions, chlorinated ethene degradation occurs most frequently under anaerobic conditions via reductive dechlorination, a process that sequentially removes chlorine atoms, eventually producing ethene. Numerous studies have demonstrated that reductive dechlorination typically stalls at DCE under iron- and sulfate-reducing conditions and complete mineralization generally requires methanogenic conditions; accumulation of VC, a potent human carcinogen is common (NRC, 2000).

Biological reductive dechlorination can occur either when halorespiratory bacteria use the chlorinated ethene as an electron acceptor (Maymó-Gatell et al., 1997) or when sulfate-reducing bacteria serendipitously co-metabolize these contaminants (Cole et al., 1995; Townsend and Suflita, 1996). Abiotic reductive dechlorination of chlorinated aliphatics by solid and dissolved transition metals has also been reported, but these reactions are typically quite slow (Vogel et al., 1987 and references cited therein) and, therefore, not likely to account for a large fraction of contaminant removal in the environment.

In addition to reductive dechlorination, less chlorinated intermediates of TCE degradation (DCE and VC) can be mineralized to CO_2 under a variety of redox conditions. Mineralization has been observed in aerobic (Davis and Carpenter, 1990), manganese-reducing (Bradley et al., 1998), and iron-reducing environments (Bradley and Chapelle, 1996; 1997). Finally, co-metabolic degradation may be important in some locations. Bacteria possessing genes for various monooxygenases may fortuitously transform TCE and less chlorinated intermediates during oxidation of a primary substrate; aerobic degradation has been demonstrated by methanotrophs (Alvarez-Cohen and McCarty, 1991), aromatic hydrocarbon degraders (Fan and Scow, 1993) and ammonia-oxidizing bacteria (Arciero et al., 1989). However, the conditions for these reactions generally do not naturally occur with great frequency (NRC, 2000).

Understanding that these various transformation reactions are dependent on prevailing redox conditions makes it clear why an accurate assessment of predominant terminal-electron accepting processes (TEAPs) in contaminated ground water is so important. The currently accepted method of accomplishing this couples measurement of

dissolved hydrogen with the spatial distribution of electron acceptor concentrations (i.e., ferric iron, sulfate, carbonate) and reduced products of terminal metabolism (ferrous iron, sulfide, and methane) (Chapelle et al., 1995). However, this determination is not always straightforward. Reduced products of terminal metabolism can migrate to down-gradient portions of contaminant plumes (Christensen et al., 2000), be replenished from mineral sources (Plummer et al., 1990) or confining beds (Chapelle and McMahon, 1991), or precipitate readily from solution (Cozzarelli et al., 2000). Determining predominant TEAPs can be even more complicated in ground-water systems experiencing transient flow.

Jakobsen et al. (1998) first suggested the use of TEAP energetics to ascertain which terminal metabolic reactions were energetically feasible within contaminant plumes. In their study, they used calculated in situ Gibbs free energies of reaction to demonstrate that concurrent iron and sulfate reduction, and at some points, methanogenesis, were energetically feasible in a landfill-leachate plume. This approach, previously used only in laboratory experiments, was later applied successfully at another pristine site (Jakobsen and Postma, 1999). One of the potential advantages of this approach is that it may be useful when addressing the potential for biodegradation of environmental contaminants (Christensen et al., 2000). Application of this method at other sites may provide useful information for future studies.

This study examined the effects of ground-water/surface-water interactions in a contaminated sub-arctic aquifer. A better understanding of how regular but transient influx of highly oxygenated surface water into a naturally anaerobic aquifer might affect

ground-water geochemistry and natural attenuation of chlorinated solvents and petroleum hydrocarbons at this and other similar sites is necessary. In addition, results of this investigation add to the very few field studies that use TEAP energetics to better understand microbial processes occurring in situ and how these might relate to contaminant degradation processes.

3.2. Methods

3.2.1. Site Description

Fort Wainwright is located within the Tanana-Chena Alluvium (Fig. 1a-b). Alluvial sediments are glacial outwash (Nelson, 1978) and originate from mafic (containing reduced iron and manganese) carbonate- and sulfate-bearing minerals in the Alaska Range (Downey and Sinton, 1990). Discontinuous permafrost is present throughout the region (Péwé et al., 1976) and at Fort Wainwright but was not encountered during drilling near Building 1060; where absent, the aquifer is considered unconfined. Depth to bedrock varies but is an estimated 50 m below the Chena River (Nakanishi and Lilly, 1998). Interior Alaska is semi-arid, receiving an average of 0.28 m of precipitation annually, and regional aquifer recharge is primarily from Alaska Range snowmelt carried by the Tanana River (Nelson, 1978). Less recharge occurs via the Chena River. Ground water generally flows northwest from the Tanana River towards the Chena River. Regionally, horizontal hydraulic conductivity is approximately 120 m day^{-1} (Nakanishi and Lilly, 1998) but this varies locally due to the heterogeneous nature of braided deposits of silt, sand, gravel, and cobbles. The hydraulic gradient is 1.23 mm

per m (Glass et al., 1996) although this varies locally and seasonally in response to Chena River stage elevation.

Ground water generally flows from the aquifer into the Chena River most of the year. However, as Chena River stage rises dramatically in late April to early May due to snowmelt runoff and ice jams, ground-water flow direction quickly reverses and highly oxygenated surface water recharges the aquifer (Taras and Grant, 1995). Although water table rises that accompany flow reversals are attenuated with distance from the river, they can still be as much as 50% of river stage rise at a distance of 250 m from the bank and can exceed 3 m near the river bank (Glass et al., 1996). Late-summer rainfall typically results in one or more discharge peaks although these peaks are usually not as dramatic as the hydrologic events associated with spring breakup.

3.2.2. Hydrology

In October 1996, a series of four PVC monitoring wells were installed perpendicular to the Chena River, between the riverbank and about 90 m distant along the path of inflowing surface water (Fig. 1b). Each well extended 12 m bgs and was screened (5 cm) at 8 sampling points. During installation, multiple lengths of polyethylene tubing were inserted into the well casing and positioned to collect ground water at each sampling point. Specific conductance, alkalinity, temperature, and dissolved oxygen were monitored in these wells before, during, and after spring 1997 breakup to determine when bank recharge occurred, how far surface-water penetrated the aquifer, and what effects aquifer recharge had on ground-water geochemistry.

3.2.3. Geochemistry

Before breakup in April 1997, 3 well clusters were installed within the contaminant plume (7315-7323; Fig. 1b). Each well cluster consisted of 3 wells, each located about 1 m apart, and individually screened at 6.1, 9.1, or 12.2 m bgs; screens were about 0.75 m in length. Ground-water geochemistry was monitored in these wells in April 1997 (aquifer discharge conditions), August 1997 (aquifer recharge conditions), and April 1998 (aquifer discharge conditions). Before sampling, wells were purged with a peristaltic pump until pH, temperature, specific conductance, and dissolved oxygen had stabilized. These parameters were measured with probes in a flow through cell. (Hydrolab, Corp.). Wells were pumped slowly (< 1 L min^{-1}) to minimize mixing between closely spaced sampling points.

Detailed sampling and analysis procedures have been previously described (Hinzman et al., 2000). Dissolved oxygen (DO) concentrations were determined with Winkler titrations (Hach, Co.). Ground-water samples for methane analyses were collected in triplicate from a glass sampling bulb (Supelco, Inc.) with a gas tight syringe, filtered through a sterile 0.45 μm syringe filter while injecting sample into sterile, O_2-free, stoppered serum vials. Samples were stored at 4 °C and then warmed to room temperature just before analysis by gas chromatography with flame ionization detection (GC-FID; Shimadzu) within a few days of collection. Methane concentrations were calculated using Henry's law constant, H_{CH4} (Stumm and Morgan, 1981) and previously described methods (McCarthy et al., 1998).

H_2 samples were collected with a peristaltic pump using the bubble-strip method (Chapelle and McMahon, 1991) and analyzed at ambient temperatures by gas chromatography with reduced gas detection (RGD2; Trace Analytical). Standards were prepared several times daily by diluting hydrogen (100 ppm; Scott Specialty Gases) in stoppered serum bottles containing UHP nitrogen at atmospheric pressure. Results were regressed using a linear model ($P \leq 0.05$). When collecting ground-water hydrogen samples, equilibration was assumed when two headspace samples collected at a 5-minute interval deviated < 5%. Dissolved hydrogen concentrations were calculated using the ideal gas law, Henry's law constant (H_{H2}; Stumm and Morgan, 1981) and in situ ground-water temperatures (Jakobsen et al., 1998), which ranged between about 2 and 10 °C.

Samples for sulfate, nitrate, and dissolved iron and manganese were filtered (0.45 µm) into polyethylene bottles. Sulfate samples were acidified with HNO_3 and chilled (4 °C) until analysis by ion chromatography. Nitrate samples were preserved with HCl, chilled (4 °C), and analyzed by ion chromatography. Samples for dissolved metals were acidified with HCl and chilled until analysis by inductively coupled plasma with mass spectroscopy (ICP-MS). All of these samples were sent to the USGS National Water Quality Laboratory (NWQL; Denver, CO) for analyses using previously published methods (Fishman et al., 1994). Total recoverable iron was measured on-site colorimetrically with the FerroVer method (Hach, Co.) on unfiltered samples; quantities of suspended ferric iron were estimated by difference between total and dissolved iron. Total sulfide was measured on unfiltered samples using the methylene blue method

immediately upon collection (Hach, Co.). Alkalinities were determined titrimetrically on-site.

In situ Gibbs free energies for hydrogen-oxidizing TEAPs (ΔG_r) were calculated using the equations and thermochemical data presented in Table 1. Specific activities of relevant chemical species were estimated using geochemical data collected as described above and Web-Phreeq (Saini-Eidukat and Yahin, 1999), a web-based interface to Phreeq (Parkhurst, 1995). Individual corrections for in situ temperatures were made using the Van't Hoff equation in the form:

$$\Delta G^{T2} = \frac{\Delta H°(298.15\ °K - T_2) + (T_2 \Delta G°)}{298.15\ °K} \quad (1)$$

where $\Delta G°$ is the Gibbs free energy of reaction for the given TEAP at standard temperature and pressure (STP), ΔG^{T2} is the Gibbs free energy for that TEAP at in situ ground-water temperature, $\Delta H°$ is the enthalpy of reaction at STP, and T_2 is the in situ ground-water temperature in degrees Kelvin (Stumm and Morgan, 1981). When determining whether iron or sulfate reduction was thermodynamically favorable, ΔG_r values below the reported threshold of about –7 kJ/mol were used (Hoehler et al., 1994; Westermann, 1994; Jakobsen et al., 1998); for methanogenesis, a threshold value of about –20 kJ/mol CH_4 was used (Conrad, 1999).

3.3. Results

Ground-water geochemistry was measured at monitoring wells near the Chena River before, during, and after aquifer recharge, which occurred between 29 April 1997 and 5 May 1997. Dissolved oxygen never exceeded 0.8 mg/L in ground water at 7331, located ca. 2 m from the riverbank (Fig. 2). Decreases in temperature, specific conductance and alkalinity showed that surface water influx occurred between 5.5 and 9 m bgs. Horizontal bank recharge extended at least 6.1 m but not to 30.5 m from the riverbank. At 7331 (Fig. 1b), approximately 65% of groundwater was displaced by surface water at a depth of about 7 m (Wegner, 1998; Hinzman et al., 2000; Hinzman et al., in press). This recharge event was small in comparison to other years (Nakanishi and Lilly, 1998).

Ground-water elevations at 7315 – 7323, about 90 m from the riverbank (Fig. 1b) and near the TCE contaminant source area, were monitored in August 1997 during a smaller discharge peak that occurred in response to late summer precipitation. At representative well 7320, ground-water elevations closely tracked Chena River stage (measured at permanent U.S. Geological Survey gaging station 15514000; Fig. 3a), demonstrating that even with distance, ground-water elevations respond quickly to Chena River stage changes in this highly transmissive aquifer.

At monitoring wells 7315 – 7323, quantities of suspended Fe(III) varied temporally ($P = 0.002$; Fig. 3b) and were highest during aquifer recharge in August 1997. Average concentrations at that sampling were 2.0 ± 0.26 mg/L (mean ± standard error). Dissolved Fe(II) concentrations at these wells ranged between 1.0 to 6.9 mg/L with an

average of 3.5 ± 1.5 mg/L (mean ± standard deviation) over the course of the study. Although average concentrations of Fe(II) at these wells were lower during aquifer recharge (August 1998) than when measured during aquifer discharge (April 1997 and 1998), the difference was not significant (P = 0.18). However, dissolved oxygen concentrations, although low, were significantly higher in water-table wells during aquifer recharge in August 1997 (P = 0.002; Table 2) than during aquifer discharge conditions, even though these sampling points are located well beyond the extent of surface-water influx. It seems likely that oxygenation of ground water at these sampling points occurred as ground water rose through the unsaturated zone in response to increases in Chena River stage.

Nitrate concentrations were generally below detection limits (< 0.05 – 0.07 mg/L; data not shown). Sulfate concentrations were substantial, ca. 25 mg/L when measured in April 1997 (Table 2). Low concentrations of sulfide and methane were present at all samplings (Table 2) although H_2 concentrations were generally suggestive of iron or manganese reduction (0.05 – 0.8 nM; Lovely et al., 1994). In April 1997, hydrogen concentrations at some sampling points were greatly elevated as a result of recent well installation and therefore, not usable as geochemical indicators; concentrations later stabilized at much lower levels (Table 2). Hydrogen was not measured at most wells in August 1997 due to equipment malfunction. Calculated in situ ΔG_r for iron and sulfate reduction were thermodynamically feasible at all samplings whereas methanogenesis via H_2/CO_2 was not at any sampling point (Table 3).

3.4. Discussion

Ground-water/surface-water interactions have the potential to affect physical and biologically-mediated natural attenuation processes in ground water. In addition to diluting contaminant concentrations, the influx of oxygenated surface water can slow contaminant transport into the adjacent river; the resulting oxidation may significantly affect microbial metabolic processes related to contaminant degradation. Given that plume boundaries had first stabilized and then receded well before any active treatment began, it was clear that some natural attenuation mechanisms were operating at this subarctic site.

It was hypothesized that influx of highly oxygenated surface water, which exceeded 10 mg/L at some times (data not shown), would cause oxygenation of ground water. However, this was not the case, as dissolved oxygen concentrations never exceeded 0.8 mg/L at any sampling point over the course of this study, even near the bank during aquifer recharge (Fig. 2). At other sites, dissolved oxygen has reportedly been a poor indicator of the extent of bank recharge (Heimann et al., 1997). This appeared to be true at Fort Wainwright also (Wegner, 1998;). It is likely that a combination of biological consumption and the chemical oxygen demand of reduced iron and manganese account for this. However, the peak elevation of the Chena River observed during spring 1997 breakup was substantially less than elevations observed in previous years (Nakanishi and Lilly, 1998) and surface-water influx did not penetrate very far into the aquifer.

While surface-water influx did not cause widespread aerobic conditions within the aquifer, accompanying rises in water table elevations may have affected ground-water redox chemistry. Ground-water elevations parallel stage changes of the Chena River, as seen at representative well 7320, ca. 90 m from the riverbank (Fig. 3a) and site-wide averages of suspended Fe(III) appeared to vary in response to river stage (Fig. 3b). Fe(III) concentrations remained constant over the winter of 1996/1997 when ground water was steadily discharging into the river (1996 data collected from other nearby wells not used in this study). Quantities of suspended Fe(III) had increased significantly by the August 1997 sampling, which took place during bank recharge and after repeated instances of fluctuating water tables in the preceding months (Fig. 3b). It seems likely that oxidation of dissolved ferrous iron, and possibly manganese, occurred in ground water farther from the river as anaerobic ground water rose through the unsaturated zone. This explanation is further supported by the fact that oxygen concentrations, although low, were significantly higher in shallow wells when measured during aquifer recharge. It also suggests a mechanism by which, at least in the upper portion of the aquifer, iron reduction occurs, in spite of the fact that aquifer solids do not contain significant Fe(III). In situ ΔG_r for iron reduction were favorable and, in the case of freshly precipitated $Fe(OH)_3$, values are close to the thermodynamic threshold of about –7 to –15 kJ/mol reported by others (Hoehler et al., 1998; Jakobsen et al., 1998; Jakobsen and Postma, 1999). Based upon these results, it likely that hydrogen concentrations are controlled by the bacterial reduction of freshly precipitated $Fe(OH)_3$. Although not measured, it is possible that

oxidized manganese might also have been present in ground water at this site (Table 2). Hydrogen concentrations at some wells were suggestive of manganese reduction.

In general, these data suggest that the shallow aquifer at Fort Wainwright is more oxidized than other, less hydrologically dynamic sites within the Chena Alluvium. At another site with otherwise similar geochemistry, suspended ferric iron was almost uniformly below detection limits and hydrogen concentrations were well within or above the range generally indicative of iron reduction (Richmond et al., submitted). At that site, water-table fluctuations are minor and distance from the Tanana River (3 km) is sufficiently large that influx of oxygenated surface water does not affect local geochemistry (Krumhardt, 1982).

The presence of low concentrations of methane and sulfide suggested that sulfate reduction and methanogenesis might also have occurred in Fort Wainwright ground water (Table 2) even though hydrogen concentrations were well below the ranges typically indicative of these processes. However, regionally, peat lenses and discontinuous permafrost occur throughout the area and are associated with ground-water methane (Kvenvolden and Lorenson, 1993). It seems likely that methane in Fort Wainwright ground water has diffused from peat or permafrost. Thermodynamic calculations provide support for this statement as in situ ΔG_r for methanogenesis via CO_2 reduction were positive for all samples and, therefore, not energetically feasible. If methanogenesis occurred, it would have done so in stagnant portions of the aquifer where hydrogen concentrations were higher or via interspecies hydrogen transfer.

However, ΔG_r values for sulfate reduction are highly favorable, suggesting that measured sulfides are the result of local production. It has been unequivocally demonstrated in laboratory experiments that hydrogen concentrations characteristic of various TEAPs are significantly influenced by temperature and electron acceptor concentrations (Westerman, 1994; Hoehler et al., 1998). Low temperatures, such as those observed at this and other subarctic sites, appear to have a large effect, enabling sulfate reduction and methanogenesis to occur at hydrogen partial pressures characteristic of iron or manganese reduction. Concurrent iron and sulfate reduction has been reported at numerous sites (Christensen et al., 2000 and references cited therein). In the presence of ferrous iron, sulfide is rapidly precipitated as FeS_2. Thus, low sulfide concentrations are not necessarily evidence for lack of sulfate reduction. Through the combined use of field measurements, laboratory microcosm studies and mineral analyses, Cozzarelli et al. (2000) showed that a lack of sulfide accumulation produced during sulfate reduction could be attributable to precipitation of ferrous sulfide. In addition, they demonstrated that concurrent sulfate reduction and methanogenesis occurred in a contaminant plume with hydrogen concentrations characteristic of iron reduction.

The fact that sulfate reduction likely occurs in ground water at Fort Wainwright, although perhaps at low rates, partially explains how reductive dechlorination could have occurred as these processes frequently co-occur (NRC, 2000). Although not spilled at this site, *cis*-DCE has been detected and in some cases, concentrations have increased, within the contaminant plume (Hinzman et al., 2000; Richmond and Braddock, submitted). The presence of the *cis* isomer in greater concentrations than the *trans* isomer provides further

evidence that biological reductive dechlorination occurred (NRC, 2000). Assuming a chloride concentration of 3.5 mg/L and previous concentrations of TCE and DCE of 120 and 40 µg/L, respectively, (Hinzman et al., 2000; Richmond and Braddock, submitted), reductive dechlorination of TCE is highly favorable at this site with ΔG_r of about −170 kJ/mol. As of this writing, the minimum energy requirements for this reaction are unknown, however, Yang and McCarty (1998) reported a minimum energy yield of −115.5 kJ/mol for reductive dechlorination of *cis*-DCE to VC. Additionally, dehalorespiration has been reported to occur at a threshold hydrogen concentration of <0.3 nM (Löffler et al., 1999). Although a mechanism by which reductive dechlorination might have occurred in ground water at this site is unidentified, it appears that conditions necessary for this process to occur were sufficient.

Stabilization of plume boundaries and decreasing contaminant concentrations provide solid evidence that natural attenuation of petroleum hydrocarbons and chlorinated solvents occurred in ground water at this subarctic site. Likely mechanisms include biological degradation (Hinzman et al., 2000; Richmond and Braddock, submitted), dilution through advective transport and mixing of ground and surface water, and the physical displacement of contaminated ground water during surface-water influx. Seasonal replenishment of ferric iron due to surface water influx and fluctuating water tables provided a means by which iron reduction could occur in this aquifer, creating conditions suitable for the degradation of a wide variety of petroleum hydrocarbons and less chlorinated TCE degradation intermediates. Although sulfate reduction likely occurred, results were not conclusive as to the extent or importance of this process.

However, conditions were sufficient to allow reductive dechlorination to proceed in spite of seasonal oxidation of ground water. Results of this study add to a growing body of knowledge describing how ground-water/surface-water interactions affect contaminant fate and transport.

3.5. Acknowledgments

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3.6. Literature Cited

Alvarez-Cohen, L., McCarty, P.L., 1991. Effects of toxicity, aeration, and reductant supply on trichloroethylene transformation by a mixed methanotrophic culture. Appl. Environ. Microbial. 57, 228-235.

Arciero, D., Vanelli, T., Logan, M., Hooper, A.B., 1989. Degradation of trichloroethylene by the ammonia-oxidizing bacterium *Nitrosomonas europaea*. Biochem. Biophys. Res. Commun. 159, 640-643.

Beller, H.R., Grbić-Galić, D., Reinhard, M., 1992. Microbial degradation of toluene under sulfate-reducing conditions and the influence of iron on the process. Appl. Environ. Microbiol. 58, 3192-3195.

Bradley, P.M., Chapelle, F.H., 1996. Anaerobic mineralization of vinyl chloride in Fe(III)-reducing aquifer sediments. Environ. Sci. Technol. 30, 2084-2086.

Bradley, P.M., Chapelle, F.H., 1997. Kinetics of DCE and VC mineralization under methanogenic and Fe(III)-reducing conditions. Environ. Sci. Technol. 31, 2692-2696.

Bradley, P.M., Landmeyer, J.E., Dinicola, R.S., 1998. Anaerobic oxidation of [1,2- ^{14}C] dichloroethene under Mn(IV)-reducing conditions. Appl. Environ. Microbiol. 64, 1560-1562.

Chapelle, F.H., McMahon, P.B., 1991. Geochemistry of dissolved inorganic carbon in a Coastal Plain aquifer. 1. Sulfate from confining beds as an oxidant in microbial CO_2 production. J. Hydrol. 127, 85-108.

Chapelle, F.H., McMahon, P.B., Dubrovsky, N.M., Fujii, R.F., Oaksford, E.T., Vroblesky, D.A., 1995. Deducing the distribution of terminal electron-accepting processes in hydrologically diverse groundwater systems. Water Resourc. Res. 31, 359-371.

Christensen, T.H., Bjerg, P.L., Banwert, S.A., Jakobsen, R., Heron, G., and Albrechtsen, H.-J., 2000. Characterization of redox conditions in ground water contaminant plumes. J. Contam. Hydrol. 45, 165-241.

Cole, J.R., Fathepure, B.Z., Tiedje, J.M., 1995. Tetrachloroethene and 3-chlorobenzoate activities are co-induced in *Desulfonamile tiedjei* DCB-1. Biodegradation. 6, 167-172.

Conrad, R., 1999. Contribution of hydrogen to methane production and control of hydrogen concentrations in methanogenic soils and sediments. FEMS Microbiol. Ecol. 28, 193-202.

Cozzarelli, I.M., Suflita, J.M., Ulrich, G.A., Harris, S.H., Scholl, M.A., Schlottmann, J.L., Christenson, S., 2000. Geochemical and microbiological methods for evaluating anaerobic processes in an aquifer contaminated by landfill leachate. Environ. Sci. Technol. 34, 4025-4033.

Davis, J.W., Carpenter, C.L., 1990. Aerobic biodegradation of vinyl chloride in groundwater samples. Appl. Environ. Microbiol. 56, 3878-3880.

Downey, J.S., Sinton, P.O., 1990. Geohydrology and ground-water geochemistry at a sub-arctic landfill, Fairbanks, Alaska. U.S. Geological Survey Water-Resources Investigations Report 90-4022.

Evans, P.J., Mang, D.T., Kim, K.S., Young, L.Y., 1991a. Anaerobic degradation of toluene by a denitrifying bacterium. Appl. Environ. Microbiol. 57, 1139-1145.

Evans, P.J., Mang, D.T., Kim, K.S., Young, L.Y., 1991b. Degradation of toluene and *m*-xylene and transformation of *o*-xylene by denitrifying enrichment cultures. Appl. Environ. Microbiol. 57, 450-454.

Fan, S., Scow, K.M., 1993. Biodegradation of trichloroethylene and toluene by indigenous microbial populations in soil. Appl. Environ. Microbiol. 59, 1911-1918.

Fishman, M.J., Raese, J.W., Gerlitz, C.N., Husband, R.A., 1994. U.S. Geological Survey approved inorganic and organic methods for the analysis of water and fluvial sediment, 1954-1994: U.S. Geological Survey Open-File Report 94-351.

Glass, R.L., Lilly, M.R., Meyer, D.F., 1996. Ground-water levels in an alluvial plain between the Tanana and Chena Rivers near Fairbanks, Alaska, 1986-93. U.S. Geological Survey Water-Resources Investigations Report 96-4060.

Harris, S.T., Ulrich, G.A., Suflita, J.M., 1999. Dominant terminal electron-accepting processes occurring at a landfill leachate-impacted site as indicated by field and laboratory measures. U.S. Geological Survey Water-Resources Investigations Report 99-4018C, Reston, VA.

Heider, J., Spormann, A.M., Beller, H,R., Widdel, F., 1998. Anaerobic bacterial metabolism of hydrocarbons. FEMS Microbiol. Rev. 22, 459-473.

Heimann, D.C., Richards, J.M., Wilkison, D.H., 1997. Agricultural chemicals in alluvial aquifers in Missouri after the 1993 flood. J. Environ. Qual. 26, 361-371.

Hinzman, L.D., Lilly, M.R., Braddock, J.F., McCarthy, K.A., Richmond, S.A., Wegner, M.A., 2000. Natural attenuation of chlorinated-hydrocarbon contamination at Fort Wainwright, Alaska: A hydrogeochemical and microbiological investigation. Institute for

Northern Engineering/Water and Environmental Research Center, University of Alaska Fairbanks. Report 00.02.

Hinzman, L. D., Wegner, M.A., Lilly, M.R. Hydrologic Investigations of Ground-water and Surface-water Interactions in Subarctic Alaska. Nordic Hydrol. In Press.

Hoehler, T.M., Alperin, M.J., Alberts, D.B., Martens, C.S., 1994. Field and laboratory studies of methane oxidation in anoxic marine sediment: Evidence for a methanogen-sulfate reducer consortium. Global Biogeochem. Cycles. 8, 451-463.

Hoehler, T.M., Alperin, M.J., Alberts, D.B., Martens, C.S., 1998. Thermodynamic control on hydrogen concentrations in anoxic sediments. Geochim. Cosmochim. Acta 62, 1745-1756.

Jakobsen, R., Albrechtsen, H.J., Rasmussen, M., Bay, H., Bjerg, P.L., Christensen, T.H., 1998. H_2 concentrations in a landfill leachate plume (Grindsted, Denmark): In situ energetics of terminal electron acceptor processes. Environ. Sci. Technol. 32, 2142-2148.

Jakobsen, R., Postma, D., 1999. Redox zoning, rates of sulfate reduction and interactions with Fe-reduction and methanogenesis in a shallow sandy aquifer, Rømø, Denmark. Geochim. Cosmochim. Acta 63, 137-151.

Krumhardt, A.P., 1982. Hydrologic information for land-use planning, Badger Road area, Fairbanks, Alaska. U.S. Geological Survey Water Resources Investigations Report 82-4097.

Kvenvolden, K.A, Lorenson, T.D., 1993. Methane in permafrost—preliminary results from coring at Fairbanks, Alaska. Chemosphere 26, 609-616.

Lendvay, J.M., Dean, S.M. Adriaens, P., 1998. Temporal and spatial trends in biogeochemical conditions at a groundwater-surface water interface: Implications for natural bioattenuation. Environ. Sci. Technol. 32, 3472-3478.

Löffler, F.E., Tiedje, J.M., Sanford, R.A., 1999. Fraction of electrons consumed in electron acceptor reduction and hydrogen thresholds as indicators of halorespiratory physiology. Appl. Environ. Microbiol. 65, 4049-4056.

Lovely, D.R., Chapelle, F.H., Woodward, J.C., 1994. Use of dissolved H_2 concentrations to determine distribution of microbially catalyzed redox reactions in anoxic ground water. Environ. Sci. Technol. 28,1205-1210.

Lovely, D.R., 1997. Potential for anaerobic bioremediation of BTEX in petroleum-contaminated aquifers. J. Indust. Microbiol. 14, 85-93.

Maymó-Gatell, X., Chien, Y., Gosset, J.M., Zinder, S.H., 1997. Isolation of a bacterium that reductively dechlorinates tetrachloroethene to ethene. Science 276, 1568-1671.

McCarthy, K.A., Lilly, M.R., Braddock, J.F., Hinzman, L.D., 1998. Natural attenuation of chlorinated-hydrocarbon contamination at Fort Wainwright, Alaska: A hydrogeochemical and microbiological investigation workplan. U.S. Geological Survey Open-File Report 98-198.

Nakanishi, A.S., Lilly, M.R., 1998. Estimate of aquifer properties by numerically simulating ground-water/surface-water interactions, Fort Wainwright, Alaska. Water-Resources Investigations Report 98-4088.

National Research Council (NRC), 1994. *Alternatives for Ground Water Cleanup.* National Academy Press, Washington, D.C.

National Research Council (NRC), 2000. Natural Attenuation for Groundwater Remediation/Committee on Intrinsic Remediation, Water Science and Technology Board [and] Board on Radioactive Waste Management, Commission on Geosciences, Environment, and Resources. National Academy Press, Wash., D.C. 274 pp.

Nelson, G.L., 1978. Hydrologic information for land-use planning, Fairbanks vicinity, Alaska. U.S. Geological Survey Open-File Report 79-959.

Parkhurst, D.L., 1995. Users Guide to PHREEQC. U.S. Geological Survey Investigative Report 95-4227.

Péwé, T.L., Bell, J.W., Forbes, R.B., Weber, F.R., 1976. Geologic map of the Fairbanks D-2 SW quadrangle, Alaska. U.S. Geological Survey Miscellaneous Investigations Series Map I-829-A, scale, 1:24,000, 1 sheet.

Plummer, L.N., Busby, J.F., Lee, R.W., Hanshaw, B.B., 1990. Geochemical modeling of the Madison aquifer in parts of Montana, Wyoming, and South Dakota. Water Resour. Res. 26, 1981-2014.

Richmond, S.A., Braddock, J.F. Geochemistry and microbiology associated with TCE transformation in treated and untreated subarctic ground water. *Submitted.*

Richmond, S.A., Lindstrom, J.E., Braddock, J.F. Assessment of natural attenuation of chlorinated aliphatics and BTEX in subarctic ground water. *Submitted.*

Saini-Eidukat, B., Yahin, A., 1999. Web-phreeq: A WWW instructional tool for modeling the distribution of chemical species in water. Computers & Geosciences, 25, 347-353.

Squillace, P.J., Thurman, E.M., 1992. Herbicide transport in rivers: Importance of hydrology and geochemistry in nonpoint-source contamination. Environ. Sci. Technol. 3, 538-545.

Squillace, P.J., Burkart, M.R., Simpkins, W.W., 1997. Infiltration of atrazine and metabolites from a stream into an alluvial aquifer. Water Resour. Bull. 33, 89-95.

Stumm, W., Morgan, J.J., 1981. *Aquatic Chemistry* (2nd ed.), John Wiley and Sons, Inc. NY, NY. 780 pp.

Taras, B.D., Grant, S.A., 1995. Continuous determination of ground water flow direction and gradient at selected sites of CERCLA concern, Fort Wainwright, Alaska, second year, first interim report. U.S. Army Cold Regions Research and Engineering. Laboratory Contract Report No. 28.

Townsend, G.T., Suflita, J.M., 1996. Characterization of chloroethylene dehalogenation by cell extracts of *Desulfomonile tiedjei* and its relationship to chlorobenzoate degradation. Appl. Environ. Microbiol. 62, 2850-2853.

U.S. Environmental Protection Agency, (U.S. EPA), 1999. Use of monitored natural attenuation at Superfund, RCRA Corrective Action, and underground storage tank sites.

Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C. Directive 9200.4-17, 32 pp.

Vogel, T.M., Grbić-Galić, D., 1986. Incorporation of oxygen from water into toluene and benzene during anaerobic fermentative transformation. Appl. Environ. Microbiol. 5, 200-202.

Vogel, T.M., Criddle, C.S., McCarty, P.L., 1987. Transformations of halogenated aliphatic compounds. Environ. Sci. Technol. 21, 722-736.

Wegner, M.A., 1998. Transient ground water and surface-water interactions at Fort Wainwright, Alaska. M.S. Thesis, University of Alaska Fairbanks, Fairbanks, Alaska, pp. 75.

Westermann, P., 1994. The effect of incubation temperature on steady-state concentrations of hydrogen and volatile fatty acids during anaerobic degradation in slurries from wetland sediments. FEMS Microbiol. Ecol. 13, 295-302.

Yang, Y., McCarty, P.L., 1998. Competition for hydrogen within a chlorinated solvent dehalogenating anaerobic mixed culture. Environ. Sci. Technol. 32, 3591-3597.

Table 3.1. Equations and thermodynamic values used for calculating in situ Gibbs free energies (ΔG_r) for H_2-oxidizing terminal-electron accepting processes (TEAPs)[a]

TEAP	Equation used for calculating in situ ΔG_r	ΔG_r^* (kJ·mol^{-1})	ΔH_r^* (kJ·mol^{-1})
$1/2H_{2(aq)} + Fe(OH)_3 + 2H^+ \rightleftharpoons Fe^{2+} + 3H_2O$	$\Delta G_r = \Delta G^{T2} + RT \ln \frac{[Fe^{2+}]}{[H_2]^{1/2}[H^+]^2}$	-100.2[b] -87.2[c]	-121.1[d]
$4H_{2(aq)} + SO_4^{2-} + H^+ \rightleftharpoons HS^- + 4H_2O$	$\Delta G_r = \Delta G^{T2} + RT \ln \frac{[HS^-]}{[H_2]^4[SO_4^{2-}][H^+]}$	-264.1	-235.0
$4H_{2(aq)} + HCO_3^- + H^+ \rightleftharpoons CH_{4(aq)} + 3H_2O$	$\Delta G_r = \Delta G^{T2} + RT \ln \frac{[CH_4]}{[H_2]^4[HCO_3^-][H^+]}$	-229.3	-237.8

[a] R is the gas constant, T is the absolute temperature in K, [ ] indicate species activity or molarity. Thermodynamic data for solutes from Langmuir (1997) and Stumm and Morgan (1981). [b] slightly aged $Fe(OH)_3$; [c] freshly precipitated $Fe(OH)_3$; [d] ΔH_r^* for goethite used for calculations as ΔH_r^* for $Fe(OH)_3$ has not been determined and temperature effects are slight. Table adapted from Jakobsen et al., 1998.

Table 3.2. Concentrations of predominant TEAP indicators used for thermodynamic calculations in ground water at Fort Wainwright, Alaska, April 1997 through April 1998.

Well	Well Depth (m bgs)	DO (mg/L)	H_2 (nM)	Mn(II) (mg/L)	Fe(II) (mg/L)	Fe(III) (mg/L, suspended)	SO_4^{2-} (mg/L)	HS^- (mg/L)[e]	CH_4 (µg/L)	pH
April 1997 Aquifer discharging into Chena River										
7315[a]	12.2	0.20	*6.06	1.1	3.4	<0.01	25	0.004	22.4	7.3
7316[a]	9.1	0.60	*3.40	1.3	3.3	0.7	26	0.004	27.2	7.2
7317[a]	6.1	0.05	*0.67	1.0	6.6	0.4	33	0.008	13.5	7.1
7318[b]	12.2	<0.01	*0.68	1.2	3.0	0.5	25	<0.002	<0.5	7.3
7319[b]	6.1	<0.05†	*0.11	0.8	4.7	0.3	39	0.052	41.8	7.1
7320[b]	9.1	<0.05†	*629	1.2	3.1	2.1	28	0.036	17.8	7.3
7321[c]	6.1	<0.01	*0.79	1.2	4.3	0.8	28	0.012	11.9	7.4
7322[c]	12.2	<0.01	*6.40	0.7	2.3	0.2	23	0.004	14.8	7.5
7323[c]	9.1	<0.01	*1.60	1.4	4.3	1.0	116	0.003	11.7	7.3
August 1997 Chena River recharging aquifer										
7315[a]	12.2	--	--	--	3.1	1.4	--	0.004	--	6.8
7316[a]	9.1	<0.05†	0.31	--	4.9	2.0	--	0.007		6.8
7317[a]	6.1	0.56	--	--	2.3	2.9	--	0.026	--	6.9
7318[b]	12.2	--	--	--	1.0	2.6	--	<0.002	--	7.2
7319[b]	6.1	0.73	--	--	1.6	2.0	--	<0.002	--	6.8
7320[b]	9.1	<0.05†	--	--	3.7	1.9	--	0.018	--	7.0
7321[c]	6.1	0.64	--	--	2.3	2.7	--	0.010	--	7.0
7322[c]	12.2	0.30	0.25	0.8	2.3	0.4	23	0.005	38.6	7.6
7323[c]	9.1	<0.05†	--	--	3.2	2.5	--	0.004	--	7.0
April 1998 Aquifer discharging into Chena River										
7315[a]	12.2	<0.01	0.10	--	2.7	1.3	--[d]	<0.002	43.3	7.0
7316[a]	9.1	<0.01	0.15	--	2.6	1.5	--[d]	0.010	84.6	7.0
7317[a]	6.1	<0.01	0.19	--	6.9	1.0	--[d]	0.009	92.4	6.9
7318[b]	12.2	<0.01	0.12	--	3.1	<0.01	--[d]	<0.002	42.1	7.0
7319[b]	6.1	0.05	0.09	--	2.9	0.1	--[d]	0.026	16.6	7.0
7320[b]	9.1	<0.01	0.11	--	3.9	1.0	--[d]	0.017	96.3	7.0
7321[c]	6.1	<0.01	0.06	--	2.7	2.3	--[d]	0.011	69.3	6.9
7322[c]	12.2	<0.01	0.16	--	2.6	<0.01	--[d]	0.008	42.2	7.0
7323[c]	9.1	<0.01	0.09	--	6.9	<0.01	--[d]	<0.002	54.5	6.9

*Hydrogen concentrations may be anomalously high due to recent well installation; † DO measured with probe; [a,b,c] well clusters; -- no data. [d] Average site-wide concentration (37 mg/L) from earlier sampling used for calculations. [e] if <0.002., 0.002 was used in calculation.

Table 3.3. Calculated Gibbs free energies (ΔG_r) for H_2-oxidizing terminal-electron accepting processes (TEAPs). All results are in $kJ \cdot mol^{-1}$. Bold numbers indicate that the reaction is thermodynamically feasible and may have occurred in situ.

Well	$Fe(OH)_3$[a] Reduction	$Fe(OH)_3$[b] Reduction	Sulfate Reduction	Methano-genesis
August 1997				
7316	**-29**	**-17**	**-38**	5
7322	**-23**	**-10**	**-33**	5
April 1998				
7315	**-27**	**-14**	**-30**	11
7316	**-27**	**-15**	**-30**	10
7317	**-26**	**-13**	**-32**	7
7318	**-27**	**-14**	**-32**	9
7319	**-25**	**-13**	**-22**	11
7320	**-26**	**-13**	**-25**	11
7321	**-27**	**-14**	**-21**	17
7322	**-28**	**-16**	**-32**	6
7323	**-26**	**-14**	**-30**	11

Thermochemical data for [a]freshly precipitated $Fe(OH)_3$ and [b]slightly aged $Fe(OH)_3$ used for calculations from Stumm and Morgan (1981). Other thermochemical data from Langmuir (1997).

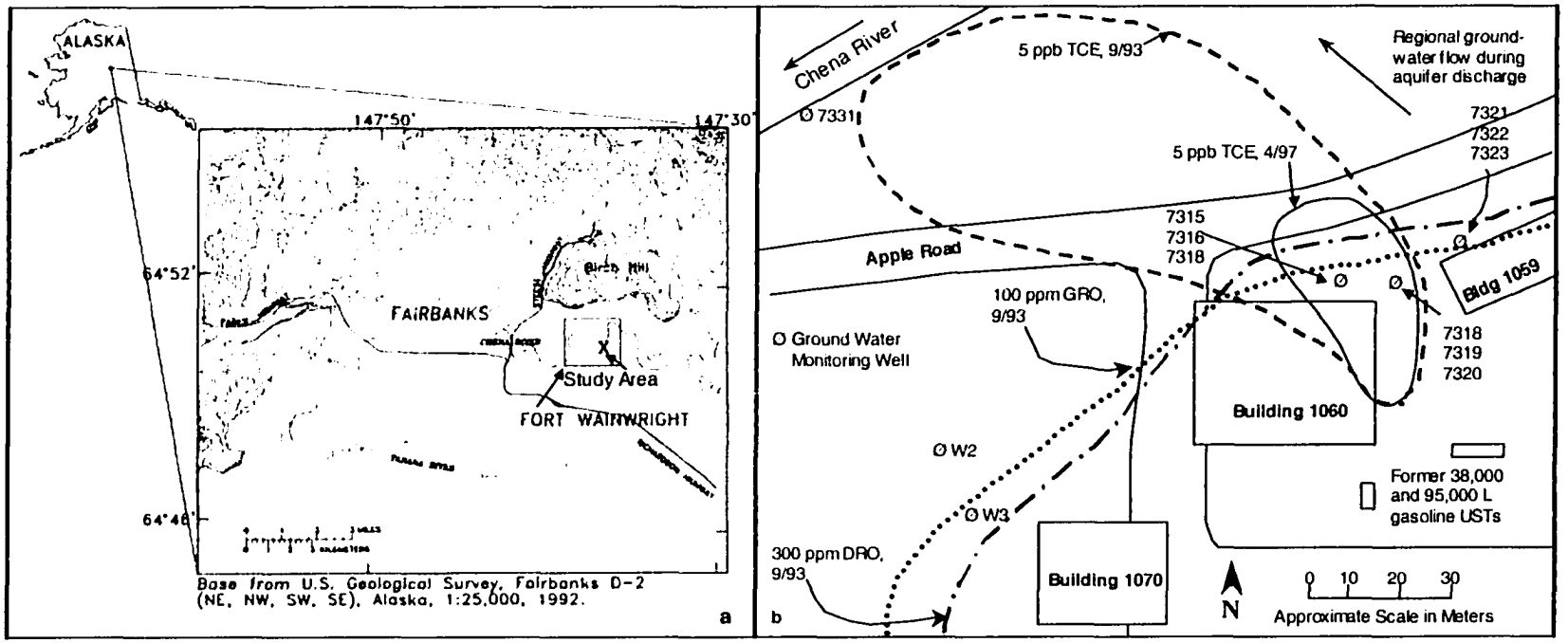

Figure 3.1. Location of study area (a) and site map (b) at Fort Wainwright, Alaska. X marks the approximate location of the study site. Monitoring wells and extent of trichloroethene (TCE), diesel- and gasoline-range organics (DRO and GRO, respectively) in ground water in 1993 and 1997 (b). By 1997, DRO and GRO had receded beyond the area shown in map. Ø monitoring well.

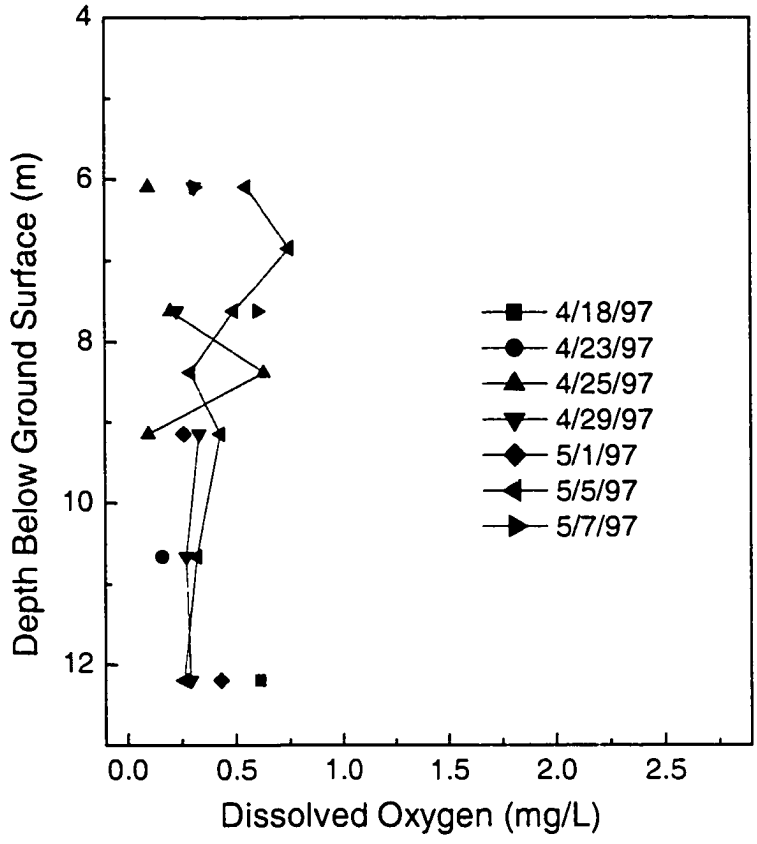

Figure 3.2. Dissolved oxygen concentrations in ground water at 7331 during bank recharge in April 1997. Monitoring well 7331 is located approximately 2 m from the riverbank.

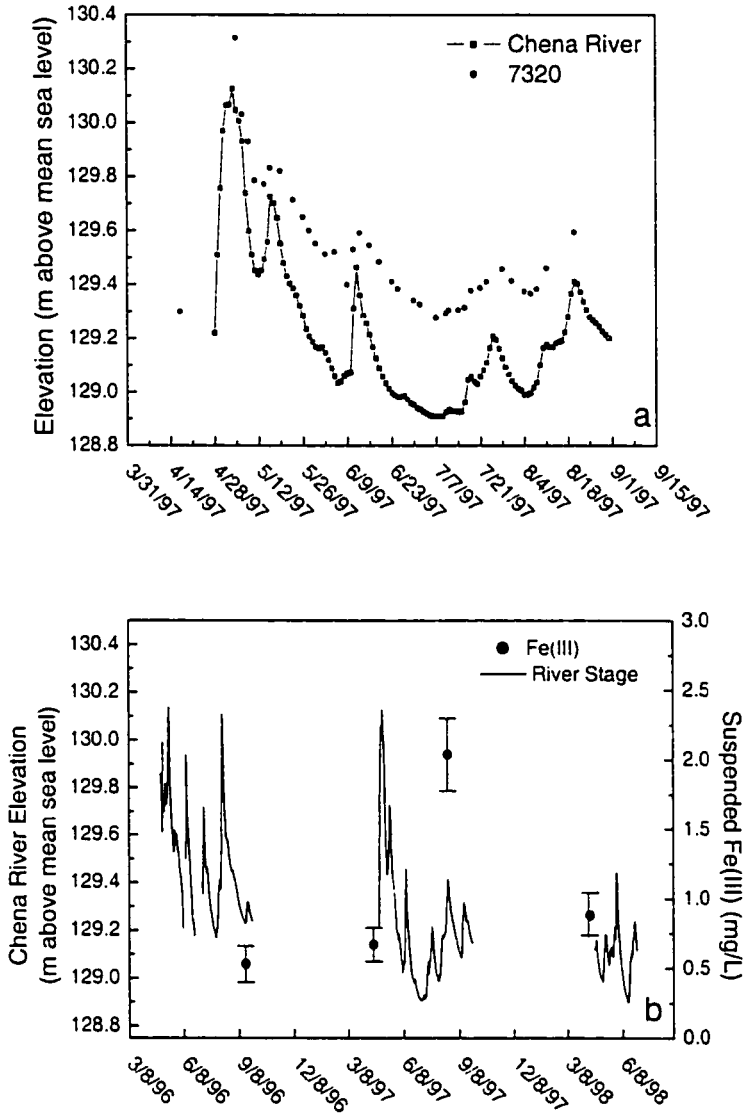

Figure 3.3. Ground-water elevations at representative monitoring well, 7320, located approximately 90 m from the riverbank (a) and suspended ferric iron in ground water, April 1997-1998 (b). Chena River stage data in (a) and (b) represent average daily values recorded by the U.S. Geological Survey at Wendell St. Bridge, Fairbanks, Alaska, the nearest continuous recording gaging station located about 2 km from Fort Wainwright.

IV. CONCLUSIONS

Documenting that natural attenuation is an effective remediation option for contaminated ground water is generally not a simple exercise; simply observing loss of contaminant, although important, is insufficient to prove bacterially-mediated contaminant degradation processes are active or that natural attenuation represents the best treatment option. A thorough understanding of local geology, hydrology, microbiology, and geochemistry is essential before useful conclusions can be drawn. The studies reported here were undertaken to better understand these processes as they relate to natural attenuation of subarctic ground water contaminated with chlorinated solvents. In addition, I evaluated currently used methods of determining TEAP distribution (e.g., distribution of hydrogen concentrations coupled with measurement of redox-sensitive species) because TEAP determinations are a critical factor when predicting the fate of ground-water contaminants.

Results of these studies showed that empirically derived ranges of hydrogen reportedly indicative of various TEAPs in temperate ground water do not accurately reflect all TEAPs in very cold subarctic ground water. At two sites within the Tanana/Chena Alluvium, ground-water hydrogen concentrations were almost uniformly within the range reported as being indicative of manganese or iron reduction in spite of the fact that aquifer minerals are mafic (containing reduced iron and manganese). However, at Fort Wainwright, substantial quantities of suspended ferric iron appeared to

vary as a result of fluctuations in ground-water elevations, which vary in response to Chena River Stage. Dissolved iron that was oxidized during transport through the unsaturated zone during stage changes is then available to support terminal metabolism by iron-reducing bacteria. At Six Mile Village, however, ferric iron was only detected in one sample and a potential source of ferric iron remains unknown at that site.

Although hydrogen concentrations were generally within or below concentrations reportedly characteristic of iron-reduction at both sites, the presence of sulfide and methane suggested that sulfate reduction and methanogenesis might have been important processes. Establishing whether these processes could occur was essential as biological reductive dechlorination occurs only under highly anaerobic conditions. To do this, I calculated in situ Gibbs free energies for individual TEAPs, as suggested by Jakobsen et al. (1998). Application of this method to local ground waters demonstrated that in addition to iron reduction, sulfate reduction was also energetically feasible. However, methanogenesis was generally not; methane present at this site probably migrated from underlying peat or permafrost. Favorable free energies for multiple TEAPs appear to be partially the result of low temperature and high sulfate concentrations (Hoehler et al., 1998).

Establishing that sulfate-reducing but not methanogenic conditions existed in ground water implied that while reductive dechlorination may have occurred (as evidenced by the presence of partially dechlorinated intermediates) conditions were not sufficiently reducing to support further dechlorination reactions and contaminants would, therefore, not undergo further microbial transformation. In addition, the fact that microbial activity in local ground water appears to be severely limited by low ambient

temperatures provides further evidence that natural attenuation may not represent the best treatment strategy at this and other permanently cold, subarctic sites. While site managers, scientists and engineers might use sound, scientifically based reasoning to determine whether natural attenuation is the most viable, economical treatment option for a particular contaminated site, they must be aware of potential community concerns when implementing this approach, particularly at sites such as Fort Wainwright and Six Mile Village, where it appears that dilution and dispersion may be the dominant contaminant-reduction processes.

LITERATURE CITED

Alvarez-Cohen, L., McCarty, P.L., 1991. Effects of toxicity, aeration, and reductant supply on trichloroethylene transformation by a mixed methanotrophic culture. Appl. Environ. Microbial. 57, 228-235.

Arciero, D., Vanelli, T., Logan, M., Hooper, A.B., 1989. Degradation of trichloroethylene by the ammonia-oxidizing bacterium *Nitrosomonas europaea*. Biochemical and Biophysical Research Communications 159, 640-643.

Atlas, R.M., 1993. *Handbook of Microbiological Media*. CRC Press, Boca Raton, FL. pp 1079.

Baedecker, M.J., Back, W. 1979a. Modern marine sediments as an analog to the chemically stressed environment of a landfill. Journal of Hydrology 43, 393-414.

Baedecker, M.J., Back, W. 1979b. Hydrogeologic processes and chemical reactions at a landfill. Ground Water 9, 429-437.

Beller, H.R., Grbić-Galić, D., Reinhard, M., 1992. Microbial degradation of toluene under sulfate-reducing conditions and the influence of iron on the process. Applied and Environmental Microbiology 58, 3192-3195.

Bjerg, P.L., Jakobsen, R., Bay, H., Rasmussen, M., Albrechtsen, H.-J., Christensen, T.H., 1997. Effects of sampling well construction on H_2 measurements made for characterization of redox conditions in a contaminated aquifer. Environmental Science and Technology 31, 3029-3031.

Braddock, J.F., Luong, H.V., Brown, E.J., 1984. Growth kinetics of *Thiobacillus ferrooxidans* isolated from arsenic mine drainage. Applied and Environmental Microbiology 48, 48-55.

Braddock, J.F., Lindstrom, J.E., Brown, E.J., 1995. Distribution of hydrocarbon-degrading microorganisms in sediments from Prince William Sound, Alaska, following the *Exxon Valdez* oil spill. Marine Pollution Bulletin 30, 125-132.

Braddock, J.F., McCarthy, K.A., 1996. Hydrologic and microbiological factors affecting persistence and migration of petroleum hydrocarbons spilled in a continuous-permafrost region. Environmental Science and Technology 30, 2626-2633.

Braddock, J.F., Catterall, P., Richmond, S.A., 1998. Assessment of the potential for biodegradation of petroleum hydrocarbons in the Railroad Industrial Area, Fairbanks, Alaska, 1993-1994. U.S. Geological Survey Open-File Report 98-287.

Braddock, J.F. and P.H. Catterall. 1999. A simple method for enumerating gasoline- and diesel-degrading microorganisms. Bioremediation Journal 3, 81-84.

Brock, T.D., Madigan, M.T., 1991. *Microbiology of Microorganisms*, 6th ed. Prentice Hall, Englewood Cliffs, NJ. 876 pp.

Broholm, M.M., Crouzet, C., Arvin, E., Cristophe, M., 2000. Concurrent nitrate and Fe(III) reduction during anaerobic biodegradation in a sandstone aquifer. Journal of Contaminant Hydrology 44, 275-300.

Brown, E.J., Resnick, S.M., Rebstock, C., Luong, H.V., Lindstrom, J.E., 1991. UAF radiorespirometric protocol for assessing hydrocarbon mineralization potential in environmental samples. Biodegradation 2, 121-127.

Bradley, P.M., Chapelle, F.H., 1996. Anaerobic mineralization of vinyl chloride in Fe(III)-reducing aquifer sediments. Environmental Science and Technology 30. 2084-2086.

Bradley, P.M., Chapelle, F.H., 1997. Kinetics of DCE and VC mineralization under methanogenic and Fe(III)-reducing conditions. Environmental Science and Technology 31, 2692-2696.

Bradley, P.M., Landmeyer, J.E., Dinicola, R.S., 1998. Anaerobic oxidation of [1,2- ^{14}C] dichloroethene under Mn(IV)-reducing conditions. Applied and Environmental Microbiology 64, 1560-1562.

Cerundolo, D.L., Coons, S.F., Gibson, E.D., Loreti, C.P., 1988. Chapter 6, *Matrix Elements and Ligands.* In: Bodek, I., Lyman, W.J., Reehl, W.F., Rosenblatt, D.H., 1988. *Environmental Inorganic Chemistry.* Pergamon Press, New York.

CH2M Hill, 1994. Building 1060 treatability study plan, delivery order 10, Fort Wainwright, Alaska.

CH2M Hill, 1996. Building 1060 treatability study annual report, year one (July 1994 to December 1995).

CH2M Hill, 1998. Building 1060 treatability study annual report, year three (January 1997 to December 1997).

Chapelle, F.H., McMahon, P.B., 1991. Geochemistry of dissolved inorganic carbon in a Coastal Plain aquifer. 1. Sulfate from confining beds as an oxidant in microbial CO_2 production. Journal of Hydrology 127, 85-108.

Chapelle, F.H., McMahon, P.B., Dubrovsky, N.M., Fujii, R.F., Oaksford, E.T., Vroblesky, D.A., 1995. Deducing the distribution of terminal electron-accepting processes in hydrologically diverse groundwater systems. Water Resources Research 31, 359-371.

Chapelle, F.H., Haack, S.K., Adriaens, P., Henry, M.A., Bradley, P.M., 1996. Comparison of E_h and H_2 measurments for delineating redox processes in a contaminated aquifer. Environmental Science and Technology 30, 3565-3569.

Christensen, T.H., Kjeldsen, P., Albrechtsen, H.-J., Heron, G., Nielsen, P.H., Bjerg, P.L., Holm, P.E., 1994. Attenuation of landfill leachate pollutants in aquifers. Critical Reviews in Environmental Science and Technology 24, 119-202.

Christensen, T.H., Bjerg, P.L., Banwert, S.A., Jakobsen, R., Heron, G., and Albrechtsen, H.-J., 2000. Characterization of redox conditions in ground water contaminant plumes. Journal of Contaminant Hydrology 45, 165-241.

Cole, J.R., Fathepure, B.Z., Tiedje, J.M., 1995. Tetrachloroethene and 3-chlorobenzoate activities are co-induced in *Desulfonamile tiedjei* DCB-1. Biodegradation. 6, 167-172.

Conrad, R., 1999. Contribution of hydrogen to methane production and control of hydrogen concentrations in methanogenic soils and sediments. FEMS Microbiology Ecology 28, 193-202.

Cozzarelli, I.M., Eganhouse, R.P., and Baedecker, M.J., 1990. Transformation of monoaromatic hydrocarbons to organic acids in anoxic ground water environment. Environmental Geology and Water Sciences 16, 135-141.

Cozzarelli, I.M., Suflita, J.M., Ulrich, G.A., Harris, S.H., Scholl, M.A., Schlottmann, J.L., Christenson, S., 2000. Geochemical and microbiological methods for evaluating anaerobic processes in an aquifer contaminated by landfill leachate. Environmental Science and Technology 34, 4025-4033.

Davis, J.W., Carpenter, C.L., 1990. Aerobic biodegradation of vinyl chloride in groundwater samples. Applied and Environmental Microbiology 56, 3878-3880.

Downey, J.S., Sinton, P.O., 1990. Geohydrology and ground-water geochemistry at a sub-arctic landfill, Fairbanks, Alaska. U.S. Geological Survey Water-Resources Investigations Report 90-4022.

Enzien, M.V., Picardal, F., Hazen, T.C., Arnold, R G., Fliermans, C.B., 1994. Reductive dechlorination of trichloroethylene and tetrachloroethylene under aerobic conditions in a sediment column. Applied and Environmental Microbiology 60, 2200-2204.

Evans, P.J., Mang, D.T., Kim, K.S., Young, L.Y., 1991a. Anaerobic degradation of toluene by a denitrifying bacterium. Applied and Environmental Microbiology 57, 1139-1145.

Evans, P.J., Mang, D.T., Kim, K.S., Young, L.Y., 1991b. Degradation of toluene and *m*-xylene and transformation of *o*-xylene by denitrifying enrichment cultures. Applied and Environmental Microbiology 57, 450-454.

Fan, S., Scow, K.M., 1993. Biodegradation of trichloroethylene and toluene by indigenous microbial populations in soil. Applied and Environmental Microbiology 59, 1911-1918.

Federal Register, 1989. Environmental Protection Agency, National Primary and Secondary Drinking Water Regulations 21, pp. 22062-22160.

Fishman, M.J., Raese, J.W., Gerlitz, C.N., Husband, R.A., 1994. U.S. Geological Survey approved inorganic and organic methods for the analysis of water and fluvial sediment, 1954-1994: U.S. Geological Survey Open-File Report 94-351.

Flynn, D.M., 1985. Hydrology and geochemical processes of a subarctic landfill, Fairbanks, Alaska: Basic data. U.S. Geological Survey Open-File Report 85-195.

Gilbert, R.O., 1987. *Statistical Methods for Environmental Pollution Monitoring*, John Wiley & Sons, Inc., New York, 320 pp.

Glass, R.L., Lilly, M.R., Meyer, D.F., 1996. Ground-water levels in an alluvial plain between the Tanana and Chena Rivers near Fairbanks, Alaska, 1986-93. U.S. Geological Survey Water-Resources Investigations Report 96-4060.

Graham, D.W., Korich, D.G., LeBlanc, R.P., Sinclair, N.A., Arnold, R.G., 1992. Applications of a colorimetric plate assay for soluble methane monooxygenase activity. Applied and Environmental Microbiology 58, 2231-2236.

Harris, S.T., Ulrich, G.A., Suflita, J.M., 1999. Dominant terminal electron-accepting processes occurring at a landfill leachate-impacted site as indicated by field and laboratory measures. U.S. Geological Survey Water-Resources Investigations Report 99-4018C, Reston, VA.

Heider, J., Spormann, A.M., Beller, H.R., Widdel, F., 1998. Anaerobic bacterial metabolism of hydrocarbons. FEMS Microbiological Reviews 22. 459-473.

Heimann, D.C., Richards, J.M., Wilkison, D.H., 1997. Agricultural chemicals in alluvial aquifers in Missouri after the 1993 flood. Journal of Environmental Quality 26, 361-371.

Henry, S.M., Grbić-Galić, D., 1989. TCE transformation by mixed and pure ground water cultures. In: Roberts, P.V., Semprini, L., Hopkins, G.D., Grbic-Galic, D., McCarty, P.L., Reinhard, M. (eds). In situ aquifer restoration of chlorinated aliphatics by methanotrophic bacteria. US Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, OK, EPA Report EPA/600/2-89/033, pp 109-125.

Hinzman, L.D., Lilly, M.R., Braddock, J.F., McCarthy, K.A., Richmond, S.A., Wegner, M.A., 2000. Natural attenuation of chlorinated-hydrocarbon contamination at Fort Wainwright, Alaska; A hydrogeochemical and microbiological investigation. Institute for Northern Engineering/Water and Environmental Research Center, University of Alaska Fairbanks. Report 00.02.

Hinzman, L.D., Wegner, M.A., Lilly, M.R. Hydrologic investigations of ground-water and surface-water interactions in subarctic Alaska. Nordic Hydrology. In press.

Hoehler, T.M., Alperin, M.J., Alberts, D.B., Martens, C.S., 1994. Field and laboratory studies of methane oxidation in anoxic marine sediment: Evidence for a methanogen-sulfate reducer consortium. Global Biogeochemical Cycles 8, 451-463.

Hoehler, T.M., Alperin, M.J., Alberts, D.B., Martens, C.S., 1998. Thermodynamic control on hydrogen concentrations in anoxic sediments. Geochimica et Cosmochimica Acta 62, 1745-1756.

Hou, C.T., Patel, R., Laskin, A.I., Barnabe, N., Bariste, I., 1983. Epoxidation of short-chain alkenes by resting-cell suspensions of propane-grown bacteria. Applied and Environmental Microbiology, 46:171-177.

Jakobsen, R., Albrechtsen, H.J., Rasmussen, M., Bay, H., Bjerg, P.L., Christensen, T.H., 1998. H_2 concentrations in a landfill leachate plume (Grindsted, Denmark): In situ energetics of terminal electron acceptor processes. Environmental Science and Technology 32, 2142-2148.

Jakobsen, R., Postma, D., 1999. Redox zoning, rates of sulfate reduction and interactions with Fe-reduction and methanogenesis in a shallow sandy aquifer, Rømø, Denmark. Geochimica et Cosmochimica Acta 63, 137-151.

Krumhardt, A.P., 1982. Hydrologic information for land-use planning, Badger Road area, Fairbanks, Alaska. U.S. Geological Survey Water Resources Investigations Report 82-4097.

Kvenvolden, K.A, Lorenson, T.D., 1993. Methane in permafrost—preliminary results from coring at Fairbanks, Alaska. Chemosphere 26, 609-616.

Langmuir, D., 1997. *Aqueous Environmental Geochemistry*. Prentice-Hall, Inc., New Jersey, 600 pp.

Lendvay, J.M., Dean, S.M. Adriaens, P., 1998. Temporal and spatial trends in biogeochemical conditions at a groundwater-surface water interface: Implications for natural bioattenuation. Environmental Science and Technology 32, 3472-3478.

Löffler, F.E., Tiedje, J.M., Sanford, R.A., 1999. Fraction of electrons consumed in electron acceptor reduction and hydrogen thresholds as indicators of halorespiratory physiology. Applied and Environmental Microbiology 65, 4049-4056.

Lovely, D.R., Goodwin, S., 1988. Hydrogen concentrations as an indicator of the predominant terminal electron-accepting reactions in aquatic sediments. Geochimica et Cosmochimica Acta 52, 2993-3003.

Lovely, D.R., Chapelle, F.H., Woodward, J.C., 1994. Use of dissolved H_2 concentrations to determine distribution of microbially catalyzed redox reactions in anoxic ground water. Environmental Science and Technology 28,1205-1210.

Lovely, D.R., 1997. Potential for anaerobic bioremediation of BTEX in petroleum-contaminated aquifers. Journal of Industrial Microbiology 14, 85-93.

Maymó-Gatell, X., Chien, Y., Gosset, J.M., Zinder, S.H., 1997. Isolation of a bacterium that reductively dechlorinates tetrachloroethene to ethene. Science 276, 1568-1671.

McCarthy, K.A., Lilly, M.R., Braddock, J.F., Hinzman, L.D., 1998. Natural attenuation of chlorinated-hydrocarbon contamination at Fort Wainwright, Alaska: A hydrogeochemical and microbiological investigation workplan. U.S. Geological Survey Open-File Report 98-198.

Nakanishi, A.S., Lilly, M.R., 1998. Estimate of aquifer properties by numerically simulating ground-water/surface-water interactions, Fort Wainwright, Alaska. Water-Resources Investigations Report 98-4088.

National Research Council (NRC), 1994. *Alternatives for Ground Water Cleanup*. National Academy Press, Washington, D.C.

National Research Council (NRC), 2000. *Natural Attenuation for Groundwater Remediation*. Committee on Intrinsic Remediation, Water Science and Technology Board [and] Board on Radioactive Waste Management, Commission on Geosciences, Environment, and Resources. National Academy Press, Wash., D.C. 274 pp.

Nelson, G.L., 1978. Hydrologic information for land-use planning, Fairbanks vicinity, Alaska. U.S. Geological Survey Open-File Report 79-959.

Oldenhuis, R., Vink, R.L.J.M., Janssen, D.B., Witholt, B., 1989. Degradation of chlorinated aliphatic hydrocarbons by *Methylosinus trichosporium* OB3b expressing soluble methane monooxygenase. Applied and Environmental Microbiology 55, 2819-2826.

Parkhurst, D.L., 1995. Users Guide to PHREEQC. U.S. Geological Survey Investigative Report 95-4227.

Péwé, T.L., Bell, J.W., Forbes, R.B., Weber, F.R., 1976. Geologic map of the Fairbanks D-2 SW quadrangle, Alaska. U.S. Geological Survey Miscellaneous Investigations Series Map I-829-A, scale, 1:24,000, 1 sheet.

Phelps, T.J., Niedzielski, J.J., Malachowsky, K.J., Schram, R.M., Herbes, S.E., White, D.C., 1991. Aerobic mineralization of vinyl chloride by a bacterium of the order Actinomycetales. Environmental Science and Technology 25, 1461-1465.

Plummer, L.N., Busby, J.F., Lee, R.W., Hanshaw, B.B., 1990. Geochemical modeling of the Madison aquifer in parts of Montana, Wyoming, and South Dakota. Water Resources Research 26, 1981-2014.

Richmond, S.A., Braddock, J.F., 2000. Geochemical characterization of anaerobic ground water in subarctic Alaska. Proceedings of the American Water Research Association Conference: Water Resources in Extreme Environments. Middleburg, Virginia, TPS-99-4, pp. 141-145.

Richmond, S.A., Lindstrom, J.E., Braddock, J.F. Assessment of natural attenuation of chlorinated aliphatics and BTEX in subarctic ground water. *Submitted.*

Richmond, S.A., Braddock, J.F. Geochemistry and microbiology associated with TCE transformation in treated and untreated subarctic ground water. *Submitted.*

Saini-Eidukat, B., Yahin, A., 1999. Web-phreeq: A WWW instructional tool for modeling the distribution of chemical species in water. Computers & Geosciences, 25, 347-353.

Shannon & Wilson, Inc., 1994. Arctic Surplus Salvage Yard, remedial investigation/feasibility study, Fairbanks, Alaska, remedial investigation report. Report prepared for the Alaska District, U.S. Army Corps of Engineers.

Shannon & Wilson, Inc., 1998. Final conceptual site model, tracts 1 and 2, Groff subdivision, Denny properties, Fairbanks, Alaska. Report prepared for the Alaska Department of Environmental Conservation, Contract 18801753.

Shannon & Wilson, Inc., 2000. Groundwater monitoring and evaluation of natural attenuation, Six Mile Richardson Highway, Fairbanks, Alaska. Prepared for the Alaska Department of Environmental Conservation.

Sorenson, K.S., Jr., Peterson, L.N., Hinchee, R.E., Ely, R.L., 2000. An evaluation of aerobic trichloroethene attenuation using first-order rate estimation. Bioremediation Journal 4, 337-357.

Squillace, P.J., Burkart, M.R., Simpkins, W.W., 1997. Infiltration of atrazine and metabolites from a stream into an alluvial aquifer. Water Resources Bulletin 33, 89-95.

Squillace, P.J., Thurman, E.M., 1992. Herbicide transport in rivers: Importance of hydrology and geochemistry in nonpoint-source contamination. Environmental Science and Technology 3, 538-545.

Stumm, W., Morgan, J.J., 1981. *Aquatic Chemistry* (2nd ed.), John Wiley and Sons, Inc. NY, NY. 780 pp.

Suarez, M.P., Rifai, H.S., 1999. Biodegradation rates for fuel hydrocarbons and chlorinated solvents in groundwater. Journal of Bioremediation 3, 337-362.

Taras, B.D., Grant, S.A., 1995. Continuous determination of ground water flow direction and gradient at selected sites of CERCLA concern, Fort Wainwright, Alaska, second year, first interim report. U.S. Army Cold Regions Research and Engineering. Laboratory Contract Report No. 28.

Townsend, G.T., Suflita, J.M., 1996. Characterization of chloroethylene dehalogenation by cell extracts of *Desulfomonile tiedjei* and its relationship to chlorobenzoate degradation. Applied and Environmental Microbiology 62, 2850-2853.

U.S. Environmental Protection Agency (U.S. EPA), 1997. *Cleaning Up the Nation's Waste Sites: Markets and Technology Trends.* 1996 edition. EPA 542-R-96-005. Washington, D.C.: EPA, Office of Solid Waste and Emergency Response.

U.S. Environmental Protection Agency, (U.S. EPA), 1999. Use of monitored natural attenuation at Superfund, RCRA Corrective Action, and underground storage tank sites. Office of Slid Waste and emergency Response, U.S. Environmental Protection Agency, Washington, D.C. Directive 9200.4-17, 32 pp.

U.S. Environmental Protection Agency (U.S. EPA), 2000. Physical-Chemical Data for Volatile Organic Compounds. http://www.epa.gov/region09/waste/sfund/prg/s5_01.htm and http://www.epa.gov/region09/waste/sfund/prg/s5_02.htm. Accessed February 2001.

Vogel, T.M. and P.L. McCarty. 1985. Biotransformation of tetrachloroethylene to trichloroethylene, dichloroethylene, vinyl chloride, and carbon dioxide under methanogenic conditions. Applied and Environmental Microbiology, 49:1080-1083

Vogel, T.M., Grbić-Galić, D., 1986. Incorporation of oxygen from water into toluene and benzene during anaerobic fermentative transformation. Applied and Environmental Microbiology 5, 200-202.

Vogel, T.M., Criddle, C.S., McCarty, P.L., 1987. Transformations of halogenated aliphatic compounds. Environmental Science and Technology 21, 722-736.

Vroblesky, D.A., Bradley, P.M., Chapelle, F.H., 1996. Influence of electron donor on the minimum sulfate concentration required for sulfate reduction in a petroleum hydrocarbon-contaminated aquifer. Environmental Science and Technology 30, 1377-1381.

Wegner, M.A., 1998. Transient ground water and surface-water interactions at Fort Wainwright, Alaska. M.S. Thesis, University of Alaska Fairbanks, Fairbanks, Alaska, pp. 75.

Westermann, P., 1994. The effect of incubation temperature on steady-state concentrations of hydrogen and volatile fatty acids during anaerobic degradation in slurries from wetland sediments. FEMS Microbiology Ecology 13, 295-302.

Yang, Y., McCarty, P.L., 1998. Competition for hydrogen within a chlorinated solvent dehalogenating anaerobic mixed culture. Environmental Science and Technology 32, 3591-3597.

VI. APPENDIX

Data collected from Fort Wainwright, Alaska, September 1996—April 1998

Abbreviations used in Data Tables

mg/L	milligrams/liter
µg/L	micrograms/liter
µS/cm	microSiemens/centimeter
nM	nanomolar
NT	not tested
NC	not calculated
ERR	Dissolved oxygen measurement in error due to air within sample line
E	Estimated concentration due to matrix interference

Table A1. Field data, September 1996.

		SITE ID			
		FWM6385	FWM6386	FWM6884	FWM6885
	Sample Date:	9/19/96	9/20/96	9/20/96	9/19/96
Constituent	Sample Time:	1815	1050	1210	1356
pH	Standard Units	6.73	7.41	7.27	6.94
Temperature	deg C	9.46	8.65	7.36	5.59
Specific Conductance	uS/cm	444	456	475	447
Dissolved Oxygen, Hydrolab	mg/L	ERR	ERR	0.18	0.2
Sulfide	mg/L	<0.001	0.062	0.072	0.001
Fe(II)	mg/L	<0.01	1.2	3.1	2.68
Total Fe	mg/L	<0.01	1.47	3.4	2.82
Alkalinity, Field	mg/L as $CaCO_3$	185	161	186	216
Dissolved H_2	nM	<0.01	NT	0.2	0.9
Dissolved CH_4	μg/L	13.94	22.13	NT	9.49

Table A2. Field data, April 1997.

		SITE ID				
		FWM6385	FWM6386	FWM6884	FWM6885	FWM6885 Duplicate
	Sample Date:	04/18/97	04/18/97	04/18/97	04/19/97	04/19/97
Constituent	Sample Time:	1411	1651	1521	1656	1731
Water Temperature	Degrees C	8.06	6.47	6.06	5.18	NT
pH, WH, Field	Standard Units	5.01	6.94	6.86	7.13	NT
Specific Conductance, Field	uS/cm	481	520	482	441	NT
Alkalinity, Field	mg/L as $CaCO_3$	216	222	254	222	NT
Dissolved Oxygen, Winkler	mg/L	0.5	0.2	<0.01	0.05	0.15
Dissolved Oxygen, Hydrolab	mg/L	0.52	0.36	0.44	0.60	NT
Sulfide	mg/L	0.002	0.049	0.085	0.02	NT
Fe(II)	mg/L	0.09	1.6	4.3	4.3	NT
Iron, Total	mg/L	0.17	1.8	4.8	4.6	NT
Dissolved H_2	nM	0.15	0.10	<0.1	NT	NT
Dissolved CH_4	μg/L	7.4	9.3	41.1	NT	NT

		Chena River	FWM7315	FWM7316	FWM7317	FWM7318
	Sample Date:	4/18/97	04/17/97	4/17/97	4/17/97	4/17/97
Constituent	Sample Time:	1800	1951	1411	1611	1731
Water Temperature	Degrees C	-0.02	5.55	6.02	7.00	5.88
pH, WH, Field	Standard Units	6.83	6.86	6.84	6.77	6.83
Specific Conductance, Field	uS/cm	217	420	454	516	425
Alkalinity, Field	mg/L as $CaCO_3$	94	193.2	218.6	246.8	200.0
Dissolved Oxygen, Winkler	mg/L	8.15	0.2	0.6	0.05	<0.01
Dissolved Oxygen, Hydrolab	mg/L	7.49	0.25	0.54	0.27	0.18
Sulfide	mg/L	<0.001	0.004	0.004	0.008	0.001
Ferrous Iron, Total	mg/L	0.29	3.4	3.3	6.6	3.0
Iron, Total	mg/L	1.79	3.4	4.0	7.0	3.5
Dissolved H_2	nM	NT	6.06	3.40	0.67	0.68
Dissolved CH_4	μg/L	NT	11.7	22.4	27.2	13.5

Table A2 continued. Field data, April 1997.

		FWM7319	FWM7320	FWM7321	FWM7322	FWM7323
	Sample Date:	04/17/97	04/17/97	04/18/97	04/18/97	04/18/97
Constituent	Sample Time:	1831	1901	1051	1311	1211
Water Temperature	Degrees C	7.86	7.00	4.89	4.37	5.40
pH, WH, Field	Standard Units	6.76	6.82	5.61	5.14	5.29
Specific Conductance, Field	uS/cm	506	479	478	360	651
Alkalinity, Field	mg/L as $CaCO_3$	228	230	234	168	240
Dissolved Oxygen, Winkler	mg/L	NT	NT	<0.01	<0.01	<0.01
Dissolved Oxygen, Hydrolab	mg/L	0.52	0.34	0.24	0.25	0.41
Sulfide	mg/L	0.052	0.036	0.012	0.004	0.003
Ferrous Iron, Total	mg/L	4.7	3.1	4.3	2.3	4.3
Iron, Total	mg/L	5	5.2	5.1	2.5	5.3
Dissolved H_2	nM	<0.1	629.00	0.79	6.40	1.60
Dissolved CH_4	μg/L	NT	41.8	17.8	11.9	14.8

Table A3. Field data, August 1997. Hydrogen data not collected to equipment malfunction.

		SITE ID				
		FWM6385	FWM6386	FWM6884	FWM6884 Duplicate	FWM6885
	Sample Date:	08/19/97	08/20/97	08/20/97	08/20/97	09/21/97
Constituent	Sample Time:	1954	1138	1305	1300	1450
Water Temperature	Degrees C	NT	NT	NT	7.23	5.81
pH, WH, Field	Standard Units	7.07	6.93	7.30	7.22	6.99
Specific Conductance, Field	uS/cm	468	NT	NT	586	464
Alkalinity, Field	mg/L as $CaCO_3$	208	178	188	182	214
Dissolved Oxygen, Winkler	mg/L	0.75	<0.01	NT	<0.01	NT
Dissolved Oxygen, Hydrolab	mg/L	NT	NT	NT	0.33	0.15
Sulfide	mg/L	0.004	0.035	0.030	0.026	0.004
Fe(II)	mg/L	0.03	1.66	2.2	2.0	NT
Iron, Total	mg/L	0.09	1.84	4.7	4.2	3.4
Dissolved H_2	nM	NT	NT	NT	NT	NT
Dissolved CH_4	µg/L	61.5	31.7	NT	66.7	NT

		Chena River	FWM7315	FWM7316	FWM7317	FWM7318	FWM7319
	Sample Date:	08/19/97	08/20/97	08/20/97	08/20/97	08/20/97	08/20/97
Constituent	Sample Time:	1440	1318	1442	1540	1620	1700
Water Temperature	Degrees C	NA	6.84	7.76	9.45	7.61	10.22
pH, WH, Field	Standard Units	7.53	6.81	6.79	6.91	7.17	6.77
Specific Conductance, Field	uS/cm	NA	439	486	581	445	550
Alkalinity, Field	mg/L as $CaCO_3$	70	172	248	194	204	208
Dissolved Oxygen, Winkler	mg/L	NT	NT	NT	NT	NT	NT
Dissolved Oxygen, Hydrolab	mg/L	NT	NT	0.4	0.65	ERR	0.73
Sulfide	mg/L	0.001	0.004	0.007	0.026	0.001	0.001
Fe(II)	mg/L	0.62	3.1	4.9	2.3	1.0	1.4
Iron, Total	mg/L	0.00	4.5	6.9	5.2	3.6	12.3
Dissolved H_2	nM	NT	NT	NT	NT	NT	NT
Dissolved CH_4	µg/L	NT	NT	NT	NT	NT	NT

Table A3 continued. Field data, August 1997.

		FWM7319 Duplicate	FWM7320	FWM7321	FWM7322	FWM7323	Equipment Blank
	Sample Date:	08/20/97	08/20/97	09/21/97	08/19/97	09/21/97	8/19/97
Constituent	Sample Time:	1705	1751	1106	1941	1128	1510
Water Temperature	Degrees C	NT	8.09	6.19	6.31	7.13	NT
pH, WH, Field	Standard Units	7.54	7.00	7.00	7.62	6.98	6.19
Specific Conductance, Field	uS/cm	NT	533	495	346	608	NT
Alkalinity, Field	mg/L as $CaCO_3$	204	230	242	176	246	4
Dissolved Oxygen, Winkler	mg/L	NT	NT	NT	<0.01	NT	NT
Dissolved Oxygen, Hydrolab	mg/L	NT	0.49	0.64	0.64	0.17	NT
Sulfide	mg/L	0.005	0.018	0.010	0.005	0.004	0.002
Fe(II)	mg/L	1.6	3.7	2.3	2.32	3.2	0.00
Iron, Total	mg/L	3.6	5.6	5.0	2.73	5.7	0.00
Dissolved H_2	nM	NT	NT	NT	NT	NT	NT
Dissolved CH_4	μg/L	NT	NT	NT	38.6	NT	NT

Table A4. Field data, April 1998. *Air injection operating; dissolved oxygen values correct.

		SITE ID					
		FWM6385	FWM6386	FWM6884	FWM6884	Chena River	FWM7315
	Sample Date:	04/17/98	04/17/98	04/17/98	04/17/98	04/16/98	04/16/98
Constituent	Sample Time:	1141	1431	1251	1301	1741	1358
Water Temperature	Degrees C	8.93	9.15	8.07	NT	0.22	7.72
pH, WH, Field	Standard Units	6.72	6.99	6.96	6.72	7.27	7.03
Specific Conductance, Field	uS/cm	489	506	502	NT	215	428
Alkalinity, Field	mg/L as $CaCO_3$	239	173	184	187	88.0	206
Dissolved Oxygen, Winkler	mg/L	0.2	1.35*	1.9*	NT	10.85	<0.01
Dissolved Oxygen, Hydrolab	mg/L	1.06	2.23	2.13	NT	17.7	0.90
Sulfide	mg/L	0.003	0.003	0.046	0.044	0.002	<0.001
Fe(II)	mg/L	0.34	0.69	1.17	0.98	0.08	2.7
Iron, Total	mg/L	0.38	0.88	1.14	1.12	0.47	4.0
Dissolved H_2	nM	0.1	0.09	0.11	NT	NT	0.095
Dissolved CH_4	µg/L	54.8	6.5	9.2	NT	NT	43.3

		FWM7315 Duplicate	FWM7316	FWM7317	FWM7318	FWM7319	FWM7320
	Sample Date:	04/16/98	4/16/98	4/16/98	04/15/98	04/16/98	04/16/98
Constituent	Sample Time:	1411	1559	1459	1931	1855	1251
Water Temperature	Degrees C	NT	8.62	8.77	7.63	9.27	8.51
pH, WH, Field	Standard Units	NT	7.00	6.92	7.00	7.02	6.98
Specific Conductance, Field	uS/cm	NT	459	540	443	500	493
Alkalinity, Field	mg/L as $CaCO_3$	209	224	251	214	210	234
Dissolved Oxygen, Winkler	mg/L	NT	<0.01	<0.01	<0.01	0.05	<0.01
Dissolved Oxygen, Hydrolab	mg/L	NT	1.34	1.25	1.29	1.03	0.93
Sulfide	mg/L	0.001	0.010	0.009	<0.001	0.026	0.017
Fe(II)	mg/L	2.3	2.6	6.9	3.07	2.9	3.9
Iron, Total	mg/L	4.0	4.1	8.6	3.1	3.0	4.9
Dissolved H_2	nM	NT	0.15	0.19	0.12	0.09	0.11
Dissolved CH_4	µg/L	NT	84.6	92.4	42.1	16.6	96.3

Table A4 continued. Field data, April 1998.

		FWM7321	FWM7322	FWM7323
	Sample Date:	04/15/98	04/15/98	04/16/98
Constituent	Sample Time:	1530	1311	1130
Water Temperature	Degrees C	7.9	6.45	6.85
pH, WH, Field	Standard Units	6.94	7.03	6.92
Specific Conductance, Field	uS/cm	497	381	573
Alkalinity, Field	mg/L as $CaCO_3$	239	174	242
Dissolved Oxygen, Winkler	mg/L	<0.01	<0.01	<0.01
Dissolved Oxygen, Hydrolab	mg/L	1.36	1.19	1.53
Sulfide	mg/L	0.011	0.008	0.001
Fe(II)	mg/L	2.70	2.47	6.3
Iron, Total	mg/L	5.00	2.57	6.9
Dissolved H_2	nM	0.06	0.16	0.09
Dissolved CH_4	μg/L	69.3	42.2	54.5

Table A5. Concentrations of inorganic compounds in ground-water samples analyzed at the U.S. Geological Survey National Water Quality Laboratory, September 1996.

		SITE ID				
		FWM6385	FWM6386	FWM6884	FWM6885	Equipment Blank
	Sample Date:	09/19/96	09/20/96	09/20/96	09/19/96	09/19/96
Constituent	Sample Time:	1815	1050	1210	1356	1820
Turbidity	NTU	5.00	NT	NT	NT	NT
pH, WH, Laboratory	Standard Units	6.9	7.4	7.3	7.0	7.2
Nitrogen Ammonia D.	mg/L as N	0.02	0.12	0.16	0.05	<0.015
Nitrogen, Nitrite D.	mg/L as N	0.01	0.02	0.02	0.01	<0.01
$NO_2 + NO_3$, Dissolved	mg/L as N	3.60	0.16	0.08	0.09	0.08
Phosphorus Ortho D.	mg/L as P	<0.01	0.02	0.03	0.01	<0.01
Carbon Organic Total	mg/L as C	2.7	18.0	5.9	NT	NT
Hardness Total	mg/L as $CaCO_3$	210	230	240	210	NT
Calcium Dissolved	mg/L as Ca	61	69	70	61	0.02
Magnesium Dissolved	mg/L as Mg	13	14	15	14	<0.01
Sodium Dissolved	mg/L as NT	7.5	7.0	7.1	5.7	<0.2
Sodium Adsorption R.	Ratio	0.2	0.2	0.2	0.2	NT
Sodium, Percent	Percent	8	7	6	6	NT
Potassium Dissolved	mg/L as K	4.7	4.8	4.5	4.0	<0.1
Chloride Dissolved	mg/L as Cl	3.5	6.5	4.1	4.0	<0.1
Sulfate Dissolved	mg/L as SO_4	34	63	62	23	<0.1
Fluoride Dissolved	mg/L as F	0.20	0.20	0.20	0.20	<0.1
Silica Dissolved	mg/L as SiO_2	19	14	16	24	<0.1
Iron Dissolved	µg/L as Fe	NT	1200	3400	3400	NT
Manganese Dissolved	µg/L as Mn	NT	210	470	670	NT
Residue Dissolved 180C	mg/L	318	352	344	302	30
Dissolved Solids Sum	mg/L	270	285	295	270	NT
Bromide Dissolved	mg/L as Br	NT	<0.01	0.13	0.03	NT
Specific Contuctance, Lab	µS/cm	456	473	480	460	2
Alkalinity, Lab	mg/L as $CaCO_3$	186	173	186	216	1

Table A6. Concentrations of inorganic compounds in ground-water samples analyzed at the U.S. Geological Survey National Water Quality Laboratory, April 1997.

		SITE ID				
		FWM6385	FWM6386	FWM6884	FWM6885	FWM6885 Duplicate
	Sample Date:	04/18/97	04/18/97	04/18/97	04/19/97	04/19/97
Constituent	Sample Time:	1411	1651	1521	1656	1731
Water Temperature	Degrees C	8.06	6.47	6.06	5.18	5.18
Turbidity	NTU	NT	NT	NT	NT	NT
pH, WH, Laboratory	Standard Units	7.3	NT	7.5	7.3	7.0
Nitrogen Ammonia D.	mg/L as N	0.04	NT	0.2	0.09	0.08
Nitrogen, Nitrite D.	mg/L as N	<0.01	NT	<0.01	<0.01	<0.01
$NO_2 + NO_3$, Dissolved	mg/L as N	1.10	NT	<0.05	<0.05	<0.05
Phosphorus, Ortho D.	mg/L as P	<0.01	NT	<0.01	0.02	0.02
Carbon, Organic, Total	mg/L as C	13.0	NT	5.4	NT	NT
Hardness, Total	mg/L as $CaCO_3$	230	NT	260	210	220
Calcium, Dissolved	mg/L as Ca	67	NT	75	62	64
Magnesium, Dissolved	mg/L as Mg	15	NT	17	14	14
Sodium, Dissolved	mg/L as Na	7	NT	7.5	5.5	5.5
Sodium, Adsorption R.	Ratio	0.2	NT	0.2	0.2	0.2
Sodium, Percent	Percent	7.0	NT	6.0	6.0	6.0
Potassium, Dissolved	mg/L as K	4.7	NT	4.6	3.9	4.0
Chloride, Dissolved	mg/L as Cl	3.1	NT	3.9	3.4	3.8
Sulfate, Dissolved	mg/L as SO_4	31.6	NT	38.7	25.3	26.0
Fluoride, Dissolved	mg/L as F	0.2	NT	0.1	0.1	0.1
Silica, Dissolved	mg/L as SiO_2	22.8	NT	20.0	25.4	25.3
Iron, Dissolved	µg/L as Fe	143	NT	4723	4421	4482
Manganese, Dissolved	µg/L as Mn	599	NT	874	789	807
Residue, Dissolved, 180C	mg/L	304	NT	334	286	292
Dissolved Solids, Sum	mg/L	258	NT	320	270	276
Bromide, Dissolved	mg/L as Br	0.01	NT	0.07	0.05	0.02
Specific Conductance, Lab	µS/cm	456	NT	534	412	NT
Alkalinity, Lab	mg/L as $CaCO_3$	170	NT	252	210	213

Table A6 continued. Concentrations of inorganic compounds in ground-water samples analyzed at the U.S. Geological Survey National Water Quality Laboratory, April 1997.

		FWM7315	FWM7316	FWM7317	FWM7318
	Sample Date:	04/17/97	4/17/97	4/17/97	4/17/97
Constituent	Sample Time:	1151	1411	1611	1731
Water Temperature	Degrees C	5.55	6.02	7.0	5.88
Turbidity	NTU	NT	NT	NT	NT
pH, WH, Laboratory	Standard Units	7.3	7.2	7.1	7.3
Nitrogen Ammonia D.	mg/L as N	0.08	0.08	0.14	0.07
Nitrogen, Nitrite D.	mg/L as N	<0.01	<0.01	<0.01	<0.01
$NO_2 + NO_3$, Dissolved	mg/L as N	0.08	0.07	0.07	0.07
Phosphorus, Ortho D.	mg/L as P	0.02	<0.01	<0.01	<0.01
Carbon, Organic, Total	mg/L as C	2.8	3.3	3.1	2.4
Hardness, Total	mg/L as $CaCO_3$	200	230	240	210
Calcium, Dissolved	mg/L as Ca	59	68	73	60
Magnesium, Dissolved	mg/L as Mg	12	14	15	13
Sodium, Dissolved	mg/L as Na	4.8	5.3	6.4	5.0
Sodium, Adsorption R.	Ratio	0.1	0.2	0.2	0.2
Sodium, Percent	Percent	5.0	5.0	6.0	5.0
Potassium, Dissolved	mg/L as K	4.0	4.3	4.8	4.0
Chloride, Dissolved	mg/L as Cl	3.2	3.5	4.0	3.4
Sulfate, Dissolved	mg/L as SO_4	24.7	26.3	32.7	24.9
Fluoride, Dissolved	mg/L as F	0.2	0.2	0.2	0.2
Silica, Dissolved	mg/L as SiO_2	25.4	24.6	21.5	25.7
Iron, Dissolved	µg/L as Fe	3805	4293	6699	3400
Manganese, Dissolved	µg/L as Mn	1153	1319	1027	1224
Residue, Dissolved, 180C	mg/L	261	293	328	276
Dissolved Solids, Sum	mg/L	257	283	308	263
Bromide, Dissolved	mg/L as Br	0.03	0.03	0.04	0.03
Specific Conductance, Lab	µS/cm	420	455	503	427
Alkalinity, Lab	mg/L as $CaCO_3$	198	218	238	202

Table A6 continued. Concentrations of inorganic compounds in ground-water samples analyzed at the U.S. Geological Survey National Water Quality Laboratory, April 1997.

		SITE ID				
		FWM7319	FWM7320	FWM7321	FWM7322	FWM7323
	Sample Date:	4/17/97	04/17/97	04/18/97	04/18/97	04/18/97
Constituent	Sample Time:	1931	1901	1051	1311	1211
Water Temperature	Degrees C	7.86	7.0	4.89	4.37	5.4
Turbidity	NTU	NT	NT	NT	NT	NT
pH, WH, Laboratory	Standard Units	7.1	7.3	7.4	7.6	7.3
Nitrogen Ammonia D.	mg/L as N	0.12	0.09	0.1	0.08	0.24
Nitrogen, Nitrite D.	mg/L as N	<0.01	<0.01	<0.01	<0.01	<0.01
NO_2 + NO_3, Dissolved	mg/L as N	0.07	0.07	<0.05	<0.05	<0.05
Phosphorus, Ortho D.	mg/L as P	<0.01	<0.01	<0.01	0.04	<0.01
Carbon, Organic, Total	mg/L as C	<0.1	2.8	2.3	2.0	5.4
Hardness, Total	mg/L as CaO_3	250	240	230	170	320
Calcium, Dissolved	mg/L as Ca	73	71	67	50	93
Magnesium, Dissolved	mg/L as Mg	15	15	15	12	22
Sodium, Dissolved	mg/L as NT	6.8	5.9	5.8	4.8	7.0
Sodium, Adsorption R.	Ratio	0.2	0.2	0.2	0.2	0.2
Sodium, Percent	Percent	6.0	6.0	6.0	6.0	5.0
Potassium, Dissolved	mg/L as K	4.7	4.5	0.05	3.5	4.9
Chloride, Dissolved	mg/L as Cl	3.9	3.4	3.8	2.9	4.3
Sulfate, Dissolved	mg/L as SO_4	39.2	28.0	27.8	22.5	113.5
Fluoride, Dissolved	mg/L as F	0.2	0.2	0.1	0.2	0.1
Silica, Dissolved	mg/L as SiO_2	20.0	23.0	24.5	27.9	21.9
Iron, Dissolved	µg/L as Fe	4983	5215	4777	2334	5018
Manganese, Dissolved	µg/L as Mn	819	1174	1197	729	1408
Residue, Dissolved, 180C	mg/L	306	307	305	235	436
Dissolved Solids, Sum	mg/L	307	296	289	227	417
Bromide, Dissolved	mg/L as Br	0.04	0.03	0.03	0.04	0.05
Specific Conductance, Lab	µS/cm	498	487	382	351	562
Alkalinity, Lab	mg/L as $CaCO_3$	230	231	225	167	239

Table A6 continued. Concentrations of inorganic compounds in ground-water samples analyzed at the U.S. Geological Survey National Water Quality Laboratory, April 1997.

		EQUIPMENT BLANK	EQUIPMENT BLANK	EQUIPMENT BLANK	TRIP BLANK
	Sample Date:	4/17/97	04/18/97	04/19/97	04/20/97
Constituent	Sample Time:	1511	1951	1315	0811
Water Temperature	Degrees C	NT	NT	NT	NT
Turbidity	NTU	NT	NT	NT	0.12
pH, WH, Laboratory	Standard Units	7.2	7.0	6.6	6.3
Nitrogen Ammonia D.	mg/L as N	<0.015	<0.015	<0.015	<0.015
Nitrogen, Nitrite D.	mg/L as N	<0.01	<0.01	<0.01	<0.01
$NO_2 + NO_3$, Dissolved	mg/L as N	0.06	<0.05	<0.05	<0.05
Phosphorus, Ortho D.	mg/L as P	<0.01	<0.01	<0.01	<0.01
Carbon, Organic, Total	mg/L as C	0.1	NT	NT	0.2
Hardness, Total	mg/L as $CaCO_3$	NC	NC	NC	NC
Calcium, Dissolved	mg/L as Ca	<0.02	0.03	0.13	<0.02
Magnesium, Dissolved	mg/L as Mg	<0.01	<0.01	<0.01	<0.01
Sodium, Dissolved	mg/L as Na	<0.2	<0.2	<0.2	<0.2
Sodium, Adsorption R.	Ratio	NC	NT	NT	NC
Sodium, Percent	Percent	NC	NC	NC	NC
Potassium, Dissolved	mg/L as K	<0.1	<0.1	<0.1	<0.1
Chloride, Dissolved	mg/L as Cl	<0.1	<0.1	<0.1	<0.1
Sulfate, Dissolved	mg/L as SO_4	<0.1	<0.1	<0.1	<0.1
Fluoride, Dissolved	mg/L as F	<0.1	<0.1	<0.1	<0.1
Silica, Dissolved	mg/L as SiO_2	<0.01	<0.1	<0.01	<0.01
Iron, Dissolved	µg/L as Fe	<3.0	NT	<3.0	<3.0
Manganese, Dissolved	µg/L as Mn	<1.0	NT	<1.0	<1.0
Residue, Dissolved, 180C	mg/L	6.0	<1.0	1.0	1.0
Dissolved Solids, Sum	mg/L	NC	NC	NC	NC
Bromide, Dissolved	mg/L as Br	<0.01	NT	<0.01	<0.01
Specific Conductance, Lab	µS/cm	4	2	2	<1.0
Alkalinity, Lab	mg/L as $CaCO_3$	3	1	1	1

Table A7. Concentrations of inorganic compounds in ground-water samples analyzed at the U.S. Geological Survey National Water Quality Laboratory, August 1997.

		SITE ID						
		FWM6385	FWM6386	FWM6884 Duplicate	FWM6884	FWM7322	Chena River	Eqpt Blank
	Sample Date:	08/19/97	08/20/97	08/20/97	08/20/97	08/19/97	08/18/97	08/18/97
Constituent	Sample Time:	1954	1138	1305	1300	1941	1308	1230
Water Temperature	Degrees C	NT	NT	7.0	NT	6.5	9.5	NT
Turbidity	NTU	NT	NT	NT	NT	NT	NT	NT
pH, WH, Laboratory	Standard Units	NT	7.10	NT	7.23	7.20	NT	NT
Nitrogen Ammonia D.	mg/L as N	0.02	0.19	0.13	0.15	0.06	<0.02	<0.02
Nitrogen, Nitrite D.	mg/L as N	0.018	0.27	<0.01	<0.01	<0.01	<0.01	<0.01
$NO_2 + NO_3$, Dissolved	mg/L as N	1.87	1.2	<0.05	<0.05	0.07	<0.05	<0.05
Phosphorus, Ortho D.	mg/L as P	<0.010	0.02	<0.01	<0.01	0.03	<0.01	<0.01
Carbon, Organic, Total	mg/L as C	NT	NT	NT	NT	NT	NT	NT
Hardness, Total	mg/L as CaO_3	NT	NT	NT	NT	NT	NT	NT
Calcium, Dissolved	mg/L as Ca	NT	87	84	83	52	NT	NT
Magnesium, Dissolved	mg/L as Mg	NT	20	19	19	12	NT	NT
Sodium, Dissolved	mg/L as Na	NT	7.7	7.4	7.4	4.9	NT	NT
Sodium, Adsorption R.	Ratio	NT	NT	NT	NT	NT	NT	NT
Sodium, Percent	Percent	NT	NT	NT	NT	NT	NT	NT
Potassium, Dissolved	mg/L as K	NT	4.8	4.5	4.5	3.5	NT	NT
Chloride, Dissolved	mg/L as Cl	NT	5.0	3.7	3.6	3.0	NT	NT
Sulfate, Dissolved	mg/L as SO_4	NT	110	86	85	23	NT	NT
Fluoride, Dissolved	mg/L as F	NT	0.2	0.1	0.1	0.2	NT	NT
Silica, Dissolved	mg/L as SiO_2	20	17	20	20	28	NT	NT
Iron, Dissolved	ug/L as Fe	68	1700	4900	4600	2600	NT	NT
Manganese, Dissolved	ug/L as Mn	170	710	860	860	800	NT	NT
Residue, Dissolved, 180C	mg/L	NT	408	NT	NT	240	NT	NT
Dissolved Solids, Sum	mg/L	NT	NT	379	349	NT	NT	NT
Bromide, Dissolved	mg/L as Br	0.01	0.07	<0.01	0.01	<0.01	NT	NT
Specific Conductance	uS/cm	NT	599	561	566	371	NT	NT
Alkalinity	mg/L as $CaCO_3$	NT	202	222	220	170	70	NT
Dissolved Oxygen	mg/L	NT	NT	NT	0.33	NT	9.66	NT

Table A8. Concentrations of inorganic compounds in ground-water samples analyzed at the U.S. Geological Survey National Water Quality Laboratory, April 1998.

		SITE ID					
		FWM6385	FWM6386	FWM6884	FWM6884 Duplicate	FWM7315	FWM7315 Duplicate
	Sample Date:	04/17/98	04/17/98	04/17/98	04/17/98	04/16/98	04/16/98
Constituent	Sample Time:	1451	1431	1251	1301	1358	1411
Turbidity	NTU	NT	NT	NT	NT	NT	NT
pH, WH	Standard Units	NT	NT	NT	NT	NT	NT
Nitrogen Ammonia D.	mg/L as N	0.11	0.07	0.09	0.07	0.10	0.10
Nitrogen, Nitrite D.	mg/L as N	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
$NO_2 + NO_3$, Dissolved	mg/L as N	<0.05	0.06	0.05	0.05	<0.05	<0.05
Phosphorus, Ortho D.	mg/L as P	<0.01	0.02	0.01	0.02	<0.01	<0.01

		FWM7316	FWM7317	FWM7318	FWM7319	FWM7320	FWM7321
	Sample Date:	04/16/98	04/16/98	04/15/98	04/16/98	04/16/98	04/15/98
Constituent	Sample Time:	1559	1459	1931	1855	1251	1451
Turbidity	NTU	NT	NT	NT	NT	NT	NT
pH, WH, Field	Standard Units	NT	NT	NT	7.02	6.98	6 94
Nitrogen Ammonia D.	mg/L as N	0.11	0.17	0.11	0.10	0.12	0 11
Nitrogen, Nitrite D.	mg/L as N	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
$NO_2 + NO_3$ Dissolved	mg/L as N	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Phosphorus, Ortho D.	mg/L as P	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

		FWM7322	FWM7323	FWM7070	FWM7070 Duplicate	Chena River
	Sample Date:	04/15/98	04/16/98	04/15/98	04/15/98	04/16/98
Constituent	Sample Time:	1311	1130	1621	1741	1741
Turbidity	NTU	NT	NT	NT	NT	NT
pH, WH, Field	Standard Units	7.03	6.92	7.08	NT	7.27
Nitrogen Ammonia D.	mg/L as N	0.09	0.11	0.03	0.07	0.11
Nitrogen, Nitrite D.	mg/L as N	<0.01	<0.01	<0.01	<0.01	<0.01
$NO_2 + NO_3$, Dissolved	mg/L as N	<0.05	<0.05	<0.05	<0.05	0.08
Phosphorus, Ortho D.	mg/L as P	0.2	<0.01	<0.01	0.2	0.01

Table A9. Most probable numbers of heterotrophs and gasoline, toluene, and diesel degraders in ground water, September 1996.

		SITE ID					
		FWM6385	FWM6386	FWM6884	FWM6885	FWM7070	FWM7073
	Sample Date:	9/19/96	9/20/96	9/20/96	9/19/96	9/19/96	9/20/96
Constituent	Sample Time:	1815	1050	1210	1356	1111	0920
Gasoline degraders	MPN/ml	3.62E+01	NT	NT	<2	<2	7.17E+01
Diesel degraders	MPN/ml	8.61E+01	NT	3.24E+01	1.65E+00	1.65E+00	7.08E+02
Toluene degraders	MPN/ml	2.86E+01	NT	NT	<2	8.00E+01	2.18E+01
Total Heterotrophs	MPN/ml	3.67E+05	NT	9.81E+05	2.28E+03	1.72E+02	4.89E+04

Table A10. Most probable numbers of gasoline and toluene degraders and heterotrophs in ground water (GW) and aquifer sediments (Sed), April 1997.

		SITE ID						
		FWM6385	FWM6386	FWM6884	FWM6885	FWM7315	FWM7316	FWM7317
	Sample Date:	04/18/97	04/18/97	04/18/97	04/19/97	04/17/97	4/17/97	4/17/97
Constituent	Sample Time:	1411	1651	1521	1656	1951	1411	1611
Heterotrophs-Sed	MPN/mL	NT	NT	NT	NT	NT	4.30E+04	3.10E+04
Gasoline Deg-Sed	MPN/mL	NT	NT	NT	NT	NT	2.30E+01	2.30E+01
Toluene Deg-Sed	MPN/mL	NT	NT	NT	NT	NT	2.30E+02	3.10E+01
Heterotrophs-GW	MPN/mL	8.28E+02	8.30E+05	3.00E+06	NT	2.30E+05	1.42E+06	3.80E+05
Gasoline Deg-GW	MPN/mL	<2	2.80E+01	1.31E+01	NT	5.70E+02	3.10E+03	2.30E+03
Toluene Deg-GW	MPN/mL	<2	9.30E+01	6.81E+01	NT	6.20E+02	9.30E+01	6.20E+01

		FWM7318	FWM7319	FWM7320	FWM7321	FWM7322	FWM7323
	Sample Date:	4/17/97	04/17/97	04/17/97	04/18/97	04/18/97	04/18/97
Constituent	Sample Time:	1731	1831	1901	1051	1311	1211
Heterotrophs-Sed	MPN/mL	6.20E+03	4.00E+03	4.30E+05	8.30E+03	3.10E+03	2.70E+04
Gasoline Deg-Sed	MPN/mL	2.30E+01	2.30E+01	4.30E+02	2.30E+01	2.30E+01	2.30E+01
Toluene Deg-Sed	MPN/mL	3.10E+02	2.31E+02	3.10E+02	2.31E+02	2.30E+02	2.30E+02
Heterotrophs-GW	MPN/mL	9.30E+05	2.20E+05	2.31E+06	3.10E+04	1.20E+05	4.62E+05
Gasoline Deg-GW	MPN/mL	3.10E+03	3.10E+03	4.31E+02	2.23E+03	4.30E+02	1.70E+02
Toluene Deg-GW	MPN/mL	9.30E+02	3.10E+02	1.80E+02	2.00E+00	3.10E+02	4.30E+01

Table A11. Most probable numbers of heterotrophs and gasoline degraders in ground water August 1997.

		SITE ID				
		FWM6385	**FWM6386**	**FWM6884**	**FWM7315**	**FWM7316**
	Sample Date:	08/19/97	08/20/97	08/20/97	08/20/97	08/20/97
Consitituent	Sample Time:	1951	1411	1611	1350	1731
Heterotrophs	MPN/mL	NA*	NA*	NA*	NA*	NA*
Gasoline Degraders	MPN/mL	7.31E+01	1.42E+03	9.10E+01	5.39E+01	2.74E+01

		FWM7317	**FWM7319**	**FWM7322**	**FWM7322 Duplicate**
	Sample Date:	08/19/97	08/19/97	08/19/97	08/19/97
Consitituent	Sample Time:	1831	1440	1941	1941
Heterotrophs	MPN/mL	NA*	NA*	NA*	NA*
Gasoline Degraders	MPN/mL	4.05E+01	1.67E+03	4 28E+02	3.08E+01

*NA; not available. Media was contaminated, all wells turbid.

Table A12. Most probable numbers of heterotrophs and gasoline degraders in ground water April 1998.

		SITE ID					
		FWM6385	FWM6386	FWM6884	FWM6884 Duplicate	FWM7070	Chena River
	Sample Date:	4/17/98	4/17/98	4/17/98	4/17/98	4/15/98	4/16/98
Constituent	Sample Time:	1141	1431	1251	1301	1741	1741
Heterotrophs	MPN/mL	3.80E+03	5.89E+08	4.10E+06	8.84E+08	4.16E+05	1.30E+05
Gasoline Degraders	MPN/mL	5.40E+01	1.64E+01	4.92E+02	6.22E+02	3.57E+03	1.30E+05

		FWM7315	FWM7315 Duplicate	FWM7316	FWM7317	FWM7318	FWM7319
	Sample Date:	4/16/98	4/16/98	4/16/98	4/16/98	4/15/98	4/16/98
Constituent	Sample Time:	1358	1411	1559	1459	1931	1855
Heterotrophs	MPN/mL	1.30E+05	1.50E+05	4.92E+04	1.94E+05	1.81E+05	3.09E+05
Gasoline Degraders	MPN/mL	3.88E+02	5.61E+02	2.95E+02	4.92E+02	4.83E+02	3.49E+02

		FWM7320	FWM7321	FWM7322	FWM7323
	Sample Date:	4/16/98	4/15/98	4/15/98	4/16/98
Constituent	Sample Time:	1251	1530	1311	1130
Heterotrophs	MPN/mL	2.89E+05	8.77E+04	1.28E+05	1.47E+04
Gasoline Degraders	MPN/mL	8.53E+02	6.22E+01	5.23E+02	5.40E+01

Table A13. Concentrations of organic compounds in ground-water samples analyzed at the U.S. Geological Survey National Water Quality Laboratory, September 1996.

		SITE ID				
		FWM6385	FWM6386	FWM6884	FWM6885	Equipment Blank
	Sample Date:	09/19/96	09/20/96	09/20/96	09/19/96	09/19/96
Constituent	Sample Time:	1815	1050	1210	1356	1820
Dibromochloromethane	µg/L	<0.2	<0.8	<0.4	<0.2	<0.2
Vinyl chloride	µg/L	<0.2	<0.8	<0.4	<0.2	<0.2
Trichlorofluoromethane	µg/L	<0.2	<0.8	<0.4	<0.2	<0 2
Methylene chloride	µg/L	<0.2	<0.8	<0.4	<0.2	<0.2
trans-1,2-Dichloroethene	µg/L	8.4	<0.8	0.26	1.2	<0.2
1,1-Dichloroethane	µg/L	<0.2	<0.8	<0.4	<0.2	<0.2
cis-1,2-Dichloroethene	µg/L	12.3	3.5	24.4	1.8	<0.2
Chloroform	µg/L	<0.2	<0.8	<0.4	<0.2	<0.2
Carbontetrachloride	µg/L	<0.2	<0.8	<0.4	<0.2	<0.2
Benzene	µg/L	<0.2	<0.8	<0.4	<0.2	<0.2
1,2-Dichloroethane	µg/L	<0.2	<0.8	<0.4	<0.2	<0.2
Trichloroethene	µg/L	9.0	15.7	33.1	1.2	<0.2
Dichlorodifluoromethane, Total	µg/L	<0.2	<0.8	<0.4	<0.2	<0.2
Dichloroethene, Total	µg/L	<0.2	<0.8	<0.4	<0.2	<0.2
Trichloroethane, Total	µg/L	<0.2	<0.8	<0.4	<0.2	<0.2
Dichloropropane, Total	µg/L	<0.2	<0.8	<0.4	<0.2	<0.2
Bromodichloromethane	µg/L	<0.2	<0.8	<0.4	<0.2	<0.2
Toluene	µg/L	<0.2	<0.8	<0.4	<0.2	<0.2
Tetrachloroethene	µg/L	<0.2	<0.8	<0.4	<0.2	<0.2
Chlorobenzene	µg/L	<0.2	<0.8	<0.4	<0.2	<0.2
Ethylbenzene	µg/L	<0.2	<0.8	<0.4	<0.2	<0.2
Xylenes (total)	µg/L	<0.2	<0.8	<0.4	<0.2	<0.2
Styrene	µg/L	<0.2	<0.8	<0.4	<0.2	<0.2
Bromoform	µg/L	<0.2	<0.8	<0.4	<0.2	<0.2
1,3-Dichlorobenzene (meta)	µg/L	<0.2	<0.8	<0.4	<0.2	<0.2
1,4-Dichlorobenzene (para)	µg/L	<0.2	<0.8	<0.4	<0.2	<0.2
1,2-Dichlorobenzene (ortho)	µg/L	<0.2	<0.8	<0.4	<0.2	<0.2
Methyl *tert*-butyl ether (MTBE)	µg/L	<0.2	<0.8	<0.4	<0.2	<0.2
Chloromethane	µg/L	E0.25	<0.2	E0.73	E0.32	E0.33
Chloroethane	µg/L	<0.2	<0.2	0.21	<0.2	<0.2

Table A14. Concentrations of organic compounds in ground-water samples analyzed at the U.S. Geological Survey National Water Quality Laboratory, April 1997.

		SITE ID					
		FWM6385	FWM6386	FWM6884	FWM6885	FWM6885 Duplicate	FWM7315
	Sample Date:	4/18/97	4/18/97	4/18/97	4/19/97	04/19/97	04/17/97
Constituent	Sample Time:	1411	1651	1521	1656	1731	1141
Bromodichloromethane	µg/L	<0.2	<2	<0.2	<0.2	<0.2	<0.2
Carbon tetrachloride	µg/L	<0.2	<2	<0.2	<0.2	<0.2	<0.2
1,2-Dichloroethane	µg/L	<0.2	<2	<0.2	<0.2	<0.2	<0.2
Bromoform, Total	µg/L	<0.2	<2	<0.2	<0.2	<0.2	<0.2
Chlorodibromomethane	µg/L	<0.2	<2	<0.2	<0.2	<0.2	<0.2
Chloroform, Total	µg/L	<0.2	<2	<0.2	<0.2	<0.2	<0.2
Toluene	µg/L	<0.2	<2	<0.2	<0.2	<0.2	<0.2
Benzene	µg/L	<0.2	<2	<0.2	<0.2	<0.2	0.305
Chlorobenzene	µg/L	<0.2	<2	<0.2	<0.2	<0.2	<0.2
Ethylbenzene	µg/L	<0.2	<2	<0.2	<0.2	<0.2	<0.2
Methylene chloride	µg/L	<0.2	<2	<0.2	<0.2	<0.2	<0.2
Tetrachloroethene	µg/L	<0.2	<2	<0.2	<0.2	<0.2	<0.2
Trichlorofluoromethane	µg/L	<0.2	<2	<0.2	<0.2	<0.2	<0.2
1,1-Dichloroethane	µg/L	<0 2	<2	<0.2	<0.2	<0.2	<0.2
Dichloroethene, Total	µg/L	<0.2	<2	<0.2	<0.2	<0.2	<0.2
Trichloroethane, Total	µg/L	<0.2	<2	<0.2	<0.2	<0.2	<0.2
1,2-Dichlorobenzene (ortho)	µg/L	<0.2	<2	<0.2	<0.2	<0.2	<0.2
Dichloropropane, Total	µg/L	<0.2	<2	<0.2	<0.2	<0.2	<0.2
trans-1,2-Dichloroethene	µg/L	8.6	<2	1.6	1.0	1.0	<0.2
1,3-Dichlorobenzene (meta)	µg/L	<0.2	<2	<0.2	<0.2	<0.2	<0.2
1,4-Dichlorobenzene (para)	µg/L	<0.2	<2	<0.2	<0.2	<0.2	<0.2
Dichlorodifluoromethane, Total	µg/L	<0.2	<2	<0.2	<0.2	<0.2	<0.2
Vinyl chloride	µg/L	<0.2	<2	<0.2	<0.2	<0.2	<0.2
Trichloroethene	µg/L	3.7	19.7	23.7	0.9	0.9	<0.2
cis-1,2-Dichloroethene	µg/L	11.3	31.4	44.4	1.2	1.2	<0.2
Styrene	µg/L	<0.2	<2	<0.2	<0.2	<0.2	<0.2
Freon 113 Unf Rec	µg/L	<0.2	<2	<0.2	<0.2	<0.2	<0.2
Methyl *tert*-butyl ether (MTBE)	µg/L	<0.2	<2	<0.2	<0.2	<0.2	<0.2
Xylene, Unf, Rec	µg/L	<0.2	<2	<0.2	<0.2	<0.2	<0.2

Table A14 continued. Concentrations of organic compounds in ground-water samples analyzed at the U.S. Geological Survey National Water Quality Laboratory, September 1996.

		SITE ID					
		FWM7315 Duplicate	FWM7316	FWM7317	FWM7318	FWM7319	FWM7320
	Sample Date:	04/17/97	04/17/97	04/17/97	04/17/97	04/17/97	04/17/97
Constituent	Sample Time:	1151	1411	1611	1731	1831	1901
Bromodichloromethane	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Carbon tetrachloride	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
1,2-Dichloroethane	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Bromoform, Total	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Chlorodibromomethane	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Chloroform, Total	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Toluene	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Benzene	µg/L	0.3	<0.2	<0.2	<0.2	<0.2	<0.2
Chlorobenzene	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Ethylbenzene	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Methylene chloride	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Tetrachloroethene	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Trichlorofluoromethane	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
1,1-Dichloroethane	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Dichloroethene, Total	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Trichloroethane, Total	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
1,2-Dichlorobenzene (ortho)	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Dichloropropane, Total	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
trans-1,2-Dichloroethene	µg/L	<0.2	<0.2	4.2	<0.2	7.1	<0.2
1,3-Dichlorobenzene (meta)	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
1,4-Dichlorobenzene (para)	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Dichlorodifluoromethane, Total	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Vinyl chloride	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Trichloroethene	µg/L	<0.2	0.7	4.7	<0.2	1.6	1.3
cis-1,2-Dichloroethene	µg/L	<0.2	0.3	14.0	<0.2	16.5	0.4
Styrene	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Freon 113 Unf Rec	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Methyl *tert*-butyl ether (MTBE)	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Xylene, Unf. Rec	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2

Table A14 continued. Concentrations of organic compounds in ground-water samples analyzed at the U.S. Geological Survey National Water Quality Laboratory, September 1996.

		SITE ID						
		FWM7321	FWM7322	FWM7323	Equip Blank	Equip Blank	Equip Blank	Trip Blank
	Sample Date:	04/18/97	04/18/97	04/18/97	4/17/97	04/19/97	04/18/97	04/20/97
Constituent	Sample Time:	1051	1311	1211	1511	1315	1951	0811
Bromodichloromethane	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Carbon tetrachloride	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
1,2-Dichloroethane	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Bromoform, Total	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Chlorodibromomethane	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Chloroform, Total	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Toluene	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	0.242	<0.2
Benzene	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Chlorobenzene	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Ethylbenzene	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Methylene chloride	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Tetrachloroethene	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Trichlorofluoromethane	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
1,1-Dichloroethane	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Dichloroethene, Total	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Trichloroethane, Total	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
1,2-Dichlorobenzene (ortho)	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Dichloropropane, Total	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
trans-1,2-Dichloroethene	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
1,3-Dichlorobenzene (meta)	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
1,4-Dichlorobenzene (para)	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Dichlorodifluoromethane, Total	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Vinyl chloride	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Trichloroethene	µg/L	<0.2	<0.2	0.4	<0.2	<0.2	<0.2	<0.2
cis-1,2-Dichloroethene	µg/L	0.2	<0.2	1.0	<0.2	<0.2	<0.2	<0.2
Styrene	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Freon 113 Unf Rec	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Methyl *tert*-butyl ether (MTBE)	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Xylene, Unf, Rec	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2

Table A15. Concentrations of organic compounds in ground-water samples analyzed at the U.S. Geological Survey National Water Quality Laboratory, August 1997.

		SITE ID						
		FWM6385	FWM6386	FWM6884	FWM6884 Duplicate	FWM7322	Equipment Blank	Equipment Blank
	Sample Date:	08/19/97	08/20/97	08/20/97	08/20/97	08/19/97	08/20/97	08/20/97
Constituent	Sample Time:	1954	1138	1305	1300	1941	1230	1009
Dichlorobromomethane	µg/L	<0.2	<0.8	<0.2	<0.2	<0.4	<0.2	<0.2
Carbon tetrachloride	µg/L	<0.2	<0.8	<0.2	<0.2	<0.4	<0.2	<0.2
1,2-Dichloroethane	µg/L	<0.2	<0.8	<0.2	<0.2	<0.7	<0.2	<0.2
Bromoform	µg/L	<0.2	<0.8	<0.2	<0.2	<0.4	<0.2	<0.2
Chlorodibromomethane	µg/L	<0.2	<0.8	<0.2	<0.2	<0.4	<0.2	<0.2
Chloroform	µg/L	<0.2	<0.8	<0.2	<0.2	<0.4	<0.2	<0.2
Toluene	µg/L	<0.2	<0.8	<0.2	<0.2	0.2	<0.2	<0.2
Benzene	µg/L	<0.2	<0.8	<0.2	<0.2	16.5	<0.2	<0.2
Chlorobenzene	µg/L	<0.2	<0.8	<0.2	<0.2	<0.4	<0 2	<0.2
Ethylbenzene	µg/L	<0.2	<0.8	<0.2	<0.2	<0.4	<0.2	<0.2
Methylene chloride	µg/L	<0.2	<0.8	<0.2	<0.2	<0.5	<0.2	<0.2
Tetrachloroethene	µg/L	<0.2	<0.8	<0.2	<0.2	<0.4	<0.2	<0.2
Trichlorofluoromethane	µg/L	<0.2	<0.8	<0.2	<0.2	<0.4	<0.2	<0.2
1,1-Dichloroethane	µg/L	<0.2	<0.8	<0.2	<0.2	<0.4	<0.2	<0.2
1,1-Dichloroethene	µg/L	<0.2	<0.8	<0.2	<0.2	<0.4	<0.2	<0.2
1,1,1-Trichloroethane	µg/L	<0.2	<0.8	<0.2	<0.2	<0.4	<0.2	<0.2
Benzene, o-chloro	µg/L	<0.2	<0.8	<0.2	<0.2	<0.4	<0.2	<0.2
1,2-Dichloropropane	µg/L	<0.2	<0.8	<0.2	<0.2	<0.4	<0.2	<0.2
trans-1,2-Dichloroethene	µg/L	10.3	<0.8	1.2	1.2	<0.4	<0.2	<0.2
Benzene, 1,3-dichloro	µg/L	<0.2	<0.8	<0.2	<0.2	<0.4	<0.2	<0.2
Benzene, 1,4-dichloro	µg/L	<0.2	<0.8	<0.2	<0.2	<0.4	<0.2	<0.2
Dichlorodifluoromethane	µg/L	<0.2	<0.8	<0.2	<0.2	0.3	<0.2	<0.2
Vinylchloride	µg/L	<0.2	<0.8	<0.2	<0.2	<0.4	<0.2	<0.2
Trichloroethene	µg/L	2.70	34.4	8.2	8.7	<0.4	<0.2	<0.2
cis-1,2-Dichloroethene	µg/L	13.3	3.5	11.5	6.1	<0.4	<0.2	<0.2
Styrene	µg/L	<0.2	<0.8	<0.2	<0.2	<0.4	<0.2	<0.2
Freon 113	µg/L	<0.2	<0.8	<0.2	<0.2	<0.4	<0.2	<0.2
Methyl *tert*-butyl ether (MTBE)	µg/L	<0.2	<0.8	<0.2	<0.2	<0.4	<0.2	<0.2
Xylenes (Total)	µg/L	<0.2	<2.3	<0.2	<0.2	<0.4	<0.2	<0.2

Table A16. Concentrations of organic compounds in ground-water samples analyzed at the U.S. Geological Survey National Water Quality Laboratory, April 1998.

		SITE ID					
		FWM6385	FWM6386	FWM6884	FWM6884 Duplicate	FWM7315	FWM7315 Duplicate
	Sample Date:	04/17/98	04/17/98	04/17/98	04/17/98	04/16/98	04/16/98
Constituent	Sample Time:	1141	1431	1301	1301	1358	1411
Dichlorobromomethane	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Carbon tetrachloride	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
1,2-Dichloroethane	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Bromoform	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Chlorodibromomethane	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Chloroform	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Toluene	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Benzene	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Chlorobenzene	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Ethylbenzene	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Methylene chloride	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Tetrachloroethene	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Trichlorofluoromethane	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
1,1-Dichloroethane	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
1,1-Dichloroethene	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
1,1,1-Trichloroethane	µg/L	<0.2	<0.2	<0.2	<0 2	<0.2	<0.2
Benzene, o-chloro	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
1,2-Dichloropropane	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
trans-1,2-Dichloroethene	µg/L	2.6	<0.2	0.2	0.2	<0.2	<0.2
Benzene, 1,3-dichloro	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Benzene, 1,4-dichloro	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Dichlorodifluoromethane	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Vinyl chloride	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Trichloroethene	µg/L	0.7	3.2	1.1	1.6	<0.2	<0.2
cis-1,2-Dichloroethene	µg/L	2.0	1.2	0.6	0.7	<0.2	<0.2
Styrene	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Freon 113	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Methyl *tert*-butyl ether (MTBE)	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Xylenes (Total)	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2

Table A16 continued. Concentrations of organic compounds in ground-water samples analyzed at the U.S. Geological Survey National Water Quality Laboratory, April 1998.

		FWM7316	FWM7317	FWM7318	FWM7319	FWM7320	FWM7321
	Sample Date:	04/16/98	04/16/98	04/15/98	04/16/98	04/16/98	04/15/98
Constituent	Sample Time:	1559	1459	1931	1855	1251	1451
Dichlorobromomethane	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Carbon tetrachloride	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
1,2-Dichloroethane	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Bromoform	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Chlorodibromomethane	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Chloroform	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Toluene	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Benzene	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Chlorobenzene	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Ethylbenzene	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Methylene chloride	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Tetrachloroethene	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Trichlorofluoromethane	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
1,1-Dichloroethane	µg/L	<0 2	<0.2	<0.2	<0.2	<0.2	<0.2
1,1-Dichloroethene	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
1,1,1-Trichloroethane	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Benzene, o-chloro	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
1,2-Dichloropropane	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
trans-1,2-Dichloroethene	µg/L	<0.2	4.5	<0.2	0.9	<0.2	<0.2
Benzene, 1,3-dichloro	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Benzene, 1,4-dichloro	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Dichlorodifluoromethane	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Vinyl chloride	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Trichloroethene	µg/L	0.2	1.3	<0.2	0.3	0.7	<0.2
cis-1,2-Dichloroethene	µg/L	0.3	9.0	<0.2	1.0	<0.2	<0.2
Styrene	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Freon 113	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Methyl *tert*-butyl ether (MTBE)	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Xylenes (Total)	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2

Table A16 continued. Concentrations of organic compounds in ground-water samples analyzed at the U.S. Geological Survey National Water Quality Laboratory, April 1998.

		SITE ID			
		FWM7322	FWM7323	FWM7070	Chena River
	Sample Date:	04/15/98	04/16/98	04/15/98	04/16/98
Constituent	Sample Time:	1311	1130	1741	1741
Dichlorobromomethane	µg/L	<0.2	<0.2	<0.2	<0.2
Carbon tetrachloride	µg/L	<0.2	<0.2	<0.2	<0.2
1,2-Dichloroethane	µg/L	<0.2	<0.2	<0.2	<0.2
Bromoform	µg/L	<0.2	<0.2	<0.2	<0.2
Chlorodibromomethane	µg/L	<0.2	<0.2	<0.2	<0.2
Chloroform	µg/L	<0.2	<0.2	<0.2	<0.2
Toluene	µg/L	<0.2	<0.2	<0.2	<0.2
Benzene	µg/L	<0.2	<0.2	<0.2	<0.2
Chlorobenzene	µg/L	<0.2	<0.2	<0.2	<0.2
Ethylbenzene	µg/L	<0.2	<0.2	<0.2	<0.2
Methylene chloride	µg/L	<0.2	<0.2	<0.2	<0.2
Tetrachloroethene	µg/L	<0.2	<0.2	<0.2	<0.2
Trichlorofluoromethane	µg/L	<0.2	<0.2	<0.2	<0.2
1,1-Dichloroethane	µg/L	<0.2	<0.2	<0.2	<0.2
1,1-Dichloroethene	µg/L	<0.2	<0.2	<0.2	<0.2
1,1,1-Trichloroethane	µg/L	<0.2	<0.2	<0.2	<0.2
Benzene, o-chloro	µg/L	<0.2	<0.2	<0.2	<0.2
1,2-Dichloropropane	µg/L	<0.2	<0.2	<0.2	<0.2
trans-1,2-Dichloroethene	µg/L	<0.2	<0.2	<0.2	<0.2
Benzene, 1,3-dichloro	µg/L	<0.2	<0.2	<0.2	<0.2
Benzene, 1,4-dichloro	µg/L	<0.2	<0.2	<0.2	<0.2
Dichlorodifluoromethane	µg/L	<0.2	<0.2	<0.2	<0.2
Vinyl chloride	µg/L	<0.2	<0.2	<0.2	<0.2
Trichloroethene	µg/L	<0.2	0.2	<0.2	<0.2
cis-1,2-Dichloroethene	µg/L	<0.2	0.5	<0.2	<0.2
Styrene	µg/L	<0.2	<0.2	<0 2	<0.2
Freon 113	µg/L	<0.2	<0.2	<0.2	<0.2
Methyl *tert*-butyl ether (MTBE)	µg/L	<0.2	<0.2	<0.2	<0.2
Xylenes (Total)	µg/L	<0.2	<0.2	<0.2	<0.2